PB87-218749

Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills

Engineering-Science, Inc., Cary, NC

Prepared for

Environmental Protection Agency, Washington, DC

Dec 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87 218749/AS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Washington DC 20460

EPA-340/1-85-013a
December 1985

Stationary Source Compliance Series

EPA

Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before comp

1. REPORT NO. EPA 340/1-85-031a	2.	PB87-218749
4. TITLE AND SUBTITLE Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills		5. REPORT DATE May, 1985 preparation
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) William T. Winberry, Engineering-Science		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Engineering-Science, Inc. One Harrison Park 401 Harrison Oaks Blvd. Cary, NC 27511		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3962
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Stationary Source Compliance Division (EN-341) 401 M St., S.W./Washington, D.C. 20460		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Cooperative project among EPA Regions I, III, IV, V, and VI, and SSCD. Supplement: Field Inspection Notebook for Monitoring TRS from Kraft Pulp Mills.

16. ABSTRACT

This document supports enforcement personnel in determining whether a total reduced sulfur (TRS) continuous emission monitoring (CEM) system is operating properly after initial compliance, in order to assure continuous compliance of Kraft pulp mills with TRS standards. The Kraft process, the applicable NSPS (Subpart BB), common TRS CEM systems, performance specification tests, and QA/QC are covered. Evaluation forms covering all aspects of the TRS CEM system are provided.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Monitoring Kraft Pulp Mills Continuous Emission Monitoring	Opacity Monitoring Systems Audit Procedures TRS Continuous Emissions Monitors	

18. DISTRIBUTION STATEMENT Release unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77)

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

EPA-340/1-85-013a

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Contract No. 68-02-3960
Work Assignment No. 53

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Stationary Source Compliance Division
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Washington, D.C. 20460

December 1985

DISCLAIMER

This report was furnished to the Environmental Protection Agency by Engineering-Science, 501 Willard Street, Durham, N. C., 27701 in fulfillment of Contract No. 68-02-3960, Work Assignment No. 53. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the U. S. Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

ACKNOWLEDGEMENTS

Engineering-Science expresses appreciation to Sonya Stelmack, Ken Malmberg, and Mark Siegler of the Stationary Source Compliance Division, Technical Support Branch of the U. S. Environmental Protection Agency, Washington, D. C. and Phil Schwindt, U. S. Environmental Protection Agency, Region VI, Dallas, Texas for their active interest in the project, timely suggestions, and support of this report. In particular, appreciation is given to Ashok Jain of the National Council of The Paper Industry for Air and Stream Improvement, Inc. for his thorough review and helpful comments to the preliminary draft of this manuscript. Appreciation is also given to Joyce Warren of Engineering-Science for her patience in typing and editing this manuscript.

Finally, appreciation is given to the U. S. Environmental Protection Agency, Air Pollution Training Institute (APTI), Manpower and Technical Information Branch, for their support with many of the graphics displayed in this manuscript.

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FORWARD

The main objective of the "Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills" is to support State and EPA personnel in their inspection of total reduced sulfur (TRS) continuous emission monitoring (CEM) systems. This will enable the agencies to determine: (1) that a TRS CEM system is operating properly after initial compliance; and (2) that emission control limits are accurately set.

An effort was made to provide information associated with all phases of TRS CEMs with respect to EPA activities. The material was covered in detail to provide an inspector not only with background material, but also basic guidance necessary to conduct an organized and thorough inspection of the TRS CEM system. In this effort, standard procedures have been developed and presented to aid the Agency inspector. The resource package involves three major documents. They are:

- Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills;
- Federal Regulations; and
- Field Inspection Notebook for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills.

The Technical Assistance Document covers important topics associated with NSPS Kraft pulp mills (40 CFR 60 Subpart BB). Background information has been provided to aid the inspector in evaluating not only the TRS CEM, but also source-specific quality assurance programs associated with the TRS CEM system. More importantly, evaluation forms have been provided at the end of the manual covering all aspects of a TRS CEM system. The manual is organized into twelve chapters. A brief synopsis of each chapter is provided below.

- Chapter 1.0 - Total Reduced Sulfur - The regulations affecting Kraft pulp mills are written in terms of total reduced sulfur (TRS). The objective of this chapter is to define the TRS term and to provide background information associated with its formation.

- Chapter 2.0 - Kraft Pulp Mills - Chapter 2.0 discusses the production of paper involving the Kraft, sulfite and neutral sulfite semichemical (NSSC) process. Over 80% of wood pulp produced in the United States is by the Kraft process, the major source of total reduced sulfur (TRS) emissions. Presently, there are 391 pulp mills located within the U.S. of which one-third are Kraft pulp mills. U.S. EPA Region IV contains the largest population of pulp mills (37%), with U.S. EPA Regions V, VI and X with equal population (15%). Characteristic emissions of the pulp industry coupled with its status as the 10th largest industry in the U.S. has caused the establishment of hydrogen sulfide ambient air quality standards in an effort to curtail gaseous emissions from pulp mills. The objective of this chapter is to review the production of paper, sources of TRS emissions and historical information assoicated with TRS emissions.

o Chapter 3.0 - Regulations - Through the State Implementation Plan (SIP) and New Source Performance Standards (NSPS), Kraft pulp mills are required to install, operate and maintain CEMs as part of their permit conditions. Data generated from the installed CEM "...may be used directly or indirectly for compliance determination..." as specified in 40CFR51. Additionally, those emissions in excess of a standard are reported quarterly to the regulatory authorities. NSPS standards for Kraft pulp mills were promulgated in 1978 and applied to particulate and total reduced sulfur emissions. Continuous emission monitoring was required for operations and maintenance purposes. The objective of this chapter is to review and discuss the regulations affecting Kraft pulp mills.

o Chapter 4.0 - Agency Inspection Program - The Agency inspection program was designed to provide the state inspector with information to determine a source's compliance status. Incorporating both the CEM certification activities and on-site inspections, the example inspection program involves a three phase and four level compliance program. The phase process involves: (1) administrative activities addressing source CEM application; (2) performance testing; and (3) final approval. The level program involves: (1) on-site inspection; (2) record review; (3) system audit; and (4) recertification procedures of the installed TRS CEM system. Each phase and level observation indicates whether or not the source CEM system has achieved the necessary level of compliance. This chapter will review in detail an agency-oriented CEM program.

o Chapter 5.0 - Monitoring System Instrumentation - NSPS Kraft pulp mills are required to monitor for operation and maintenance purposes. SIP standards may differ. Commercially available TRS monitors are based on the extractive technique. The main objective of an extractive system is to extract a representative sample from the source and transfer it to the detector system for analysis without compromising its integrity. Common detector systems employ either direct measurement of TRS (gas chromatography) or remove SO_2, oxidize the TRS to SO_2 and then analyze the SO_2 as TRS either by electrochemical, fluorescent, flame photometric or coulometric technique. The objective of this chapter is to describe most systems available on the market for monitoring TRS emissions.

o Chapter 6.0 - Generation of Standard Test Atmospheres - The analytical systems for monitoring total reduced sulfur (TRS) vary from gas chromatography to coulometric techniques. Varied as they are, they must all be calibrated with a standard atmosphere of pollutant so a determination of their precision and accuracy can be established. Calibration techniques involving both dynamic and static calibration systems have been used routinely in source monitoring. However, due to the complexity of the pollutant (involving a combination of four separate reduced sulfur compounds), traditional calibration techniques like the compressed gas cylinder have limited applications. Portable permeation tube calibrators appear to be the logical choice as part of an agency test system to generate standard test atmopshere used during inspection and audit procedures. The objective of this chapter is to review all systems which have the ability to generate test atmospheres of H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. The strengths and weaknesses of each method will be discussed. In addition, the correct procedure for analyzing test gas cylinders will be investigated.

- Chapter 7.0 - Comparative Studies of TRS Monitors - Analytical techniques for monitoring total reduced sulfur (TRS) from Kraft pulp mills have traditionally been associated with wet chemical extractive methods. Sampling normally involves extracting the gas through a probe and directing the sample through a conditioning system with subsequent absorption in a series of impingers. The concentration of pollutant is determined through wet chemical analysis of the impinger content. Indeed, the majority of the Federal Reference Methods applicable to stationary sources are based on wet chemistry sampling and analysis. As continuous emission monitors replace wet chemical techniques as the compliance method, the comparison between the two is inevitable. The objective of this chapter is to review available studies involving method comparisons of wet chemical techniques and TRS CEMs.

- Chapter 8.0 - The Reference Method - As defined in Subpart A-General Provisions, of 40CFR60, a "Reference Method" means any method of sampling and analyzing for an air pollutant as described in Appendix A-Reference Methods. The Reference Methods are promulgated by EPA to provide uniform analytical methods to ensure consistency and accuracy in the data generated. The legal authority for this action lies in Section 110, 111, 114 and 301 (a) of the Clean Air Act. Each Reference Method involves specifications for equipment, procedures and system performance. The objective of this chapter is to discuss the specification of Federal Reference Method 16 and Federal Reference Method 16A. In particular, method strengths and weaknesses along with required quality assurance activities will be reviewed.

- Chapter 9.0 - Performance Specification Test - After the total reduced sulfur (TRS) continuous emission monitoring (CEM) system has been purchased and installed on the source, it must pass a Performance Specification Test (PST). The intent of the PST is to provide the regulatory agency an opportunity to evaluate the installed monitoring system to ensure its initial operation. The PST is a one time certification procedure. It is not the intent of the PST to demonstrate long term performance of the monitoring system. Two PSTs apply to monitoring TRS from Kraft pulp mills:

  - Performance Specification Test 5; and
  - Performance Specification Test 3.

  The objective of this chapter is to discuss both of these PSTs as applied to Kraft pulp mills.

- Chapter 10.0 - Excess Emission Reports - EPA and many state air pollution control agencies are rapidly expanding their programs involving recordkeeping and reporting requirements in association with emission monitoring programs and performance testing. This is due, in part, to new regulations pertaining to new and existing sources as outlined in 40 CFR 60 and 40 CFR 51 respectively. These regulations require "installation of monitoring equipment and performance testing..." and "for periodic reports and recordkeeping of nature and magnitude of such emissions." Additionally, Sections 113 and 114 of the Clean Air Act (CAA) as amended in 1977 involves the use of recordkeeping and reporting requirements as a means of enforcement of emission standards. The objective of this chapter is to review the regulations associated with recordkeeping and reporting requirements for Kraft pulp mills and to recommend a standardized reporting and agency review format.

- Chapter 11.0 - Quality Assurance/Quality Control - The primary objective of quality assurance/quality control is to ensure that all data collected and reported by the TRS CEM system is meaningful, precise and accurate within a stated acceptance criteria.

As CEMs became an integral part of the enforcement activities of both EPA and Agency programs, it became imperative that some form of continued evaluation of the monitoring system occur to ensure its continued performance and reliability. This continued evaluation would assist EPA and the State in establishing CEM long-term performance and reliability as part of their data base. Consequently, QA/QC activities involve both source and agency functions. The main objective of this chapter is to address the QA/QC activities associated with:

- U. S. Environmental Protection Agency;
- Industry; and
- State Agency.

- Chapter 12.0 - Equipment Selection - The monitoring of total reduced sulfur compounds from Kraft pulp mills can be performed by either wet chemical or continuous emission monitoring instrumentation. As will be demonstrated in this manual, each method contains both strengths and weaknesses. The wet chemical techniques are simpler to use, but care must be taken during all aspects of the procedures to ensure an accurate "value". Likewise, continuous emissions monitors appear to provide accurate data if an established quality assurance program is incorporated as part of the source continuous emission monitoring program. The objective of this chapter is to provide a list of vendors to the reader to assist in the selection of a total reduced sulfur monitoring system, whether wet chemical or continuous.

- Chapter 13.0 - Bibliography - A bibliography is provided at the end of this document. It provides a source of additional information for those readers who may need a more extensive review.

- Chapter 14.0 - Index - The index is provided for the agency inspector to quickly reference topics throughout the Technical Assistance Document.

To supplement this Technical Assistance Document manual, a Field Inspection Notebook has been developed. The Field Inspection Notebook is a step-by-step procedures manual, associated with an Agency CEM program, involving the phase and level approach in inspecting TRS CEMs. It is intended to be used by the control agency inspectors, at the source, when evaluating a source CEM program involving TRS monitoring systems.

Consequently, the purpose of the Technical Assistance Document and the Field Inspection Notebook is to provide the necessary data and technical information to assist State inspectors in the evaluation of both NSPS and SIP Kraft pulp mills with respect to TRS continuous emission monitors. Utilization of these two documents will enable the State inspector to make regulatory decisions based on an understanding and systematic evaluation of a source CEM program.

1.0 TOTAL REDUCED SULFUR

1.1 INTRODUCTION

In 1675, Robert Boyle identified sulfur as an element. Sulfur is a member of the Group VI elements of the periodic table. The other members of the group are oxygen (O_2), selenium (Se), tellurium (Te) and polonium (Po). Sulfur occurs in nature in both the free state and the combined state and has been known for centuries. Although not very abundant (0.05 percent), sulfur is readily available because of its occurences in large beds of the free element. These beds, usually several hundred feet below ground, are thought to be due to bacterial decomposition of calcium sulfate. About 80 percent of the world's sulfur supply comes from deposits of native sulfur in Texas and Louisiana. Other important deposits are in the volcanic districts of Sicily, Japan and Mexico.

Sulfur occurs in the combined state, as sulfides, in the following common minerals: galena, PbS; iron pyrites, FeS_2; and argentite, Ag_2S. Deposits of gypsum, $CaSO_4 \cdot 2H_2O$, is another important sulfur product. Sulfur also occurs in the combined state in many organic substances, such as yolks of eggs and hair.

1.2 OXIDATION STATES OF SULFUR

Elemental sulfur, in the free state, has no characteristic odor. Elemental sulfur exists as a yellow crystalline rhombic solid composed of eight (8) sulfur molecules in a ring formation, as illustrated in Figure 1.1.

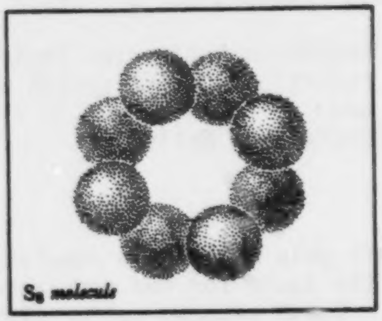

Figure 1.1. Elemental Sulfur

However, as the rhombic sulfur is heated, the rhombic crystals change to a monoclinic form which is still composed of an eight member ring, but now has a different geometric form.

As we continue to heat the sulfur, the ring structure dissociates into S_2 molecules and the color of the vapor gradually changes from clear to yellow. At temperatures of about 2000°C, S_2 molecules dissociate in the monoatomic vapor, S. With excess air present, the monoatomic S reacts with O_2 to form different oxidized compounds, such as SO_2, SO_3, and H_2SO_4.

Depletion of oxygen in the process causes the monoatomic S to combine with hydrogen (H) to form reduced sulfur compounds, such as H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. As the sulfur molecule changes, it is, in essence, changing its ability to gain or loose electrons. Each state, therefore, represents different "oxidation" states. Table 1.1 lists the differert "oxidation" states, formulas and names for sulfur.

TABLE 1.1
FORMULAS AND NAMES OF IMPORTANT SULFUR COMPOUNDS AND IONS

Names	Formulas	Electronic State	Common Name Usage
Hydrogen sulfide Sulfide ion (Hydrogen sulfide ion)	H_2S $S = (HS^-)$	-2	Reduced state
Sulfur	S_8 $(S_6S_4S_2S)$	0	Neutral state
Sulfur dioxide Sulfite ion (Hydrogen sulfite ion) Sulfurous acid	SO_2 $SO_3{=}(HSO_3-)$ H_2SO_3	+4	Oxidized state
Sulfur trioxide Sulfate ion (Hydrogen sulfate ion) Sulfuric acid	SO_3 $SO_4{=}(HSO_4^-)$ H_2SO_4	+6	

New Source Performance Standards (NSPS) address reduced sulfur limitations [as H_2S or total reduced sulfur (TRS)] in the following subparts:

- o Subpart J - Petroleum Refineries (H_2S or TRS apply only with a reduction control system not followed by incineration); and
- o Subpart BB - Kraft Pulp Mills.

1.3 TERMINOLOGY

Subpart BB - Kraft pulp mills, are regulated for TRS emissions. (Chapter 2.0 will discuss the basis for the regulations and their applicability to Kraft pulp mills). Total reduced sulfur (TRS) is a common term used by EPA to collectively regulate four major constituents of emissions from Kraft pulp mills.

TRS is defined as the sum of concentrations of the following reduced sulfur compounds present in the regulated emission point.

$$TRS = [H_2S + CH_3SH + (CH_3)_2S + (CH_3)_2S_2]$$

where:

TRS = Total reduced sulfur, in ppm, dry basis;

H_2S = Hydrogen sulfide, ppm;

CH_3SH = Methyl mercaptan, ppm;

$(CH_3)_2S$ = Dimethyl sulfide, ppm; and

$(CH_3)_2S_2$ = Dimethyl disulfide, ppm.

Early tests performed by EPA at selected Kraft pulp mills determined that these were the major reduced sulfur emissions.

1.3.1 Hydrogen Sulfide (H_2S)

Hydrogen sulfide represents the largest gaseous emission from the Kraft process. Hydrogen sulfide is formed in the recovery furnace and in the digester in a reducing atmosphere as the sulfur compounds in the black liquor are volatilized and reduced. Hydrogen sulfide is a colorless gas with an offensive odor; in fact, it is what gives rotten eggs their offensive smell. This gas is very toxic in small quantities.

1.3.2 Methyl Mercaptan (CH_3SH)

Methyl mercaptan is formed during the Kraft cooking and is present in low concentrations as a dissolved gas in the black liquor. Methyl mercaptan is formed in the digester and is primarily emitted with the digester relief and blow.

1.3.3 Dimethyl Sulfide $(CH_3)_2S$ and Dimethyl Disulfide $(CH_3)_2S_2$.

Dimethyl sulfide is primarily formed through the reaction of methyl mercaptide ion with the methoxy-lignin component of the wood. It does not, however, dissociate as hydrogen sulfide and methyl mercaptan do. Major emission point within the Kraft process is the recovery system.

2.0 PULP MILLS

2.1 PRODUCTION OF PAPER

There are two distinct phases in the conversion of raw wood into the finished paper product: (1) pulping of wood; and (2) production of paper and related products from the pulp:

- o Kraft (sulfate);
- o sulfite; or
- o neutral sulfite semichemical (NSSC).

2.1.1 Kraft (Sulfate) Process

Bark is first removed from the logs, then the peeled logs are fed into a machine which cuts them into chips. The chips are fed to a digester where the lignin that binds the wood fibers is dissolved in a solution of sodium sulfide and caustic soda. This "cooking solution" is known as the white liquor. The caustic soda enables the breakdown of lignins, under controlled conditions of temperature and pressure, to alcohols and acids, thus freeing the cellulose fibers (Figure 2.1).

This hydrolysis also produces mercaptans and sulfides, which are responsible for the malodors.

Presently, there are two types of digesters used in the pulp and paper process; batch and continuous. In recent years, more and more of the mills are using the continuous process rather than the batch process.

As the name implies, batch processing involves a fixed volume of woods chips to be processed. As the breakdown of the lignin proceeds by the white liquor, pressure builds up in the digester. It is essential that this pressure be released periodically, or continuously, to control and maintain proper operation. The uncondensibles vented during this "pressure release" step are recovered through a heat exchanger/condenser combination. At the end of the digestion, the contents are transferred to the blow tank.

In the continuous digester, a steady flow of wood chips is added to the digester. Once again, white liquor and steam are added to produce the chemical reaction. In the continuous digester configuration, the wood chips are normally pretreated in a pre-steaming vessel where they are wetted and deaerated.

At the bottom of the digester is a countercurrent wash zone where the pulp-liquor mixture is washed. The spent liquor from this "cold washing" is drawn off the bottom of the digester into a flash tank where this "black" liquor is expanded or flashed. The flash stream from the flash tank is used in the presteaming vessel. The uncondensibles from the stream are recovered by a condenser. The weak black liquor from the primary flash tank is further used in the process.

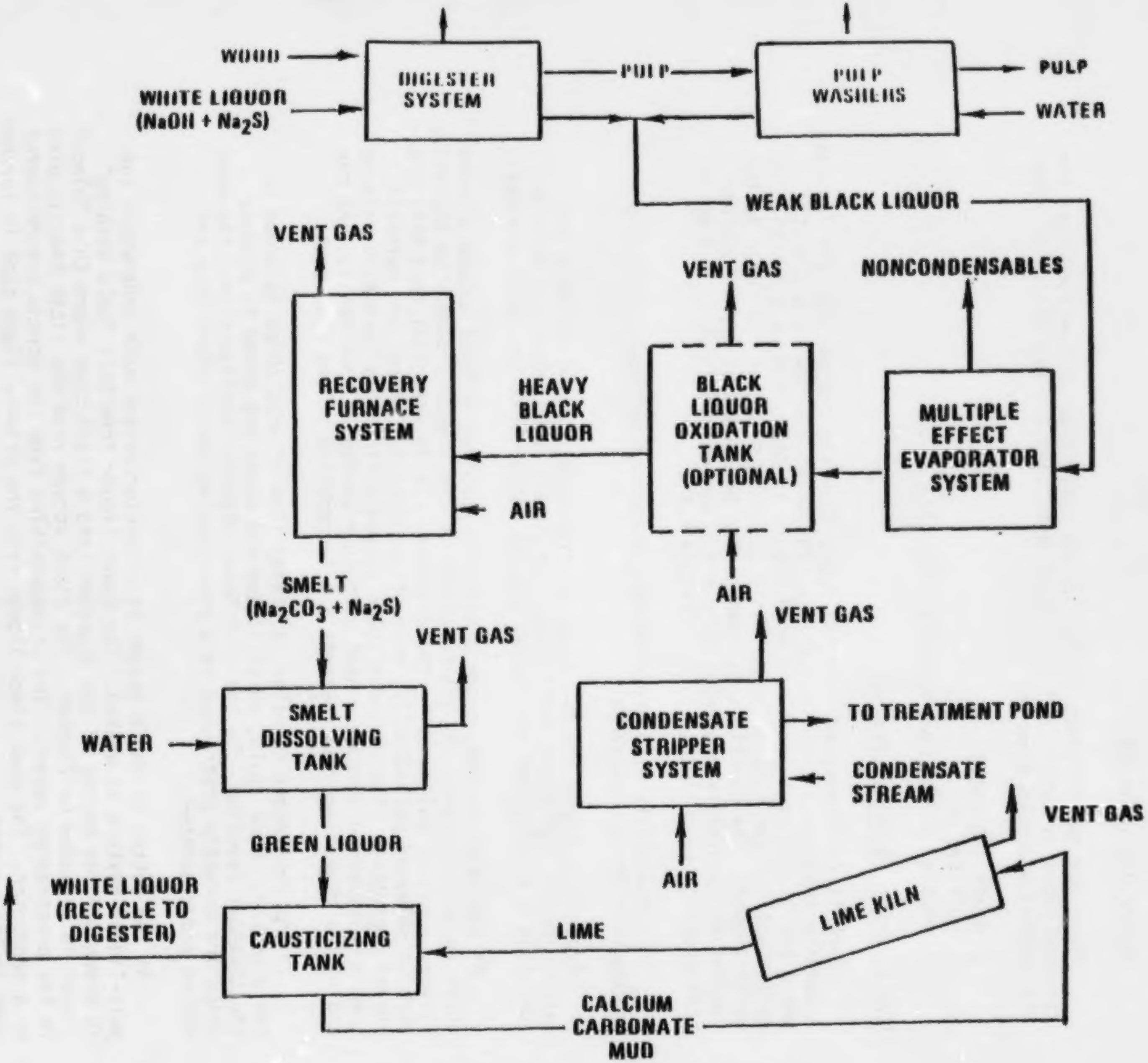
WOOD
WHITE LIQUOR (NaOH + Na2S)
DIGESTER SYSTEM
PULP
PULP WASHERS
PULP
WATER
WEAK BLACK LIQUOR
VENT GAS
RECOVERY FURNACE SYSTEM
HEAVY BLACK LIQUOR
AIR
VENT GAS
BLACK LIQUOR OXIDATION TANK (OPTIONAL)
NONCONDENSABLES
MULTIPLE EFFECT EVAPORATOR SYSTEM
AIR
SMELT (Na2CO3 + Na2S)
VENT GAS
VENT GAS
WATER
SMELT DISSOLVING TANK
CONDENSATE STRIPPER SYSTEM
TO TREATMENT POND
CONDENSATE STREAM
VENT GAS
AIR
GREEN LIQUOR
WHITE LIQUOR (RECYCLE TO DIGESTER)
CAUSTICIZING TANK
LIME
LIME KILN
CALCIUM CARBONATE MUD

Figure 2.1. Kraft Pulp Mill Operation

As the pressure in the digester is lowered, this causes the soft woods chips to explode and mat together into a fiber pulp. The "black liquor," due to the residual pressure, is forced into a blow tank as illustrated in Figure 2.1. The noncondensable gases from the digester are either confined and treated or released to the atmosphere.

The "black liquor" is diluted in the blow tank and then is pumped to washers where the black liquor is removed. There are presently two major types of washers used in the industry: rotary-drum vacuum washers and diffusion washers. Of the two, vacuum washers are the most common.

In the vacuum washer, the pulp first passes through a "knotter" where chunks of wood not cooked in the digester are removed. The pulp is then washed with water, counter currently, then dewatered on a vacuum filter, and readied for processing.

Continuous diffusion washing involves depositing the pulp in a series of screen plates, through water washing. The water leaves the wash cylinder and flows downward to the drainage system. The residual pulp is scraped from the screen plates and readied for processing.

In both processes, the pulp is washed counter currently to remove the black liquor and waste wood products. From here, the pulp may be bleached to form paper products or dried and sold as market pulp.

The remaining process involves recovering sodium and sulfur from the spent black liquor. This is accomplished through the recovery furnace system. There are two major types of recovery furnaces: (1) direct-contact system and (2) indirect-contact evaporator.

In the direct-contact system, black liquor mixed with weak liquor from the pulp washers is pumped through an oxidation tower to increase chemical recovery and odor control. This oxidation step allows the conversion of sodium sulfide to innocuous salts to prevent the release of hydrogen sulfide. At this point the solids are approximately 15%.

From the oxidation tower, the liquid passes through a multi-stage evaporator, where the solids increase to between 60-70%.

Concentration of the black liquor is necessary to facilitate combustion of the dissolved organic material in the recovery furnace.

The concentrated black liquor is then sprayed into the recovery furnace, where the organics support combustion. There are three major purposes for burning concentrated black liquor in the recovery furnace: (1) recover sodium and sulfur; (2)to produce steam and (3) dispose of unwanted dissolved wood components in the liquor.

The black liquor is introduced into the furnace through spray nozzles. Air for combustion is supplied through a forced-draft system. Part of this air is used to maintain the reducing zone at the bottom of the furnace where the char bed is converted from sodium sulfate and other sodium-base sulfur compounds to sodium sulfide. The char bed is formed from the introduction of the black liquor into the drying zone of the recovery furnace, causing the evaporation of water and formation of dry solids which fall to the bottom of the furnace to form the char bed.

The remaining forced air is used to complete oxidation of compounds above the char bed.

The release of heat from the combustion zone is sufficient to liquify the char bed, allowing it to be drained from the recovery furnace into a smelt-dissolving tank. The dissolved smelt, containing mainly sodium sulfide, sodium sulfate and sodium carbonate, is called green liquor.

Emissions of TRS from the recovery furnace and the direct contact evaporator can be high. Recovery furnace emissions are affected by distribution of combustion air, concentration of black liquor solids, spray pattern of nozzles in recovery furnace, heat content of liquor fed and sodium sulfide concentration in the black liquor.

The smelt dissolving tank, causticizer and lime kiln are all part of the closed-loop system of converting green liquor to white liquor. The process begins at the smelt dissolving tank located below the recovery furnace. Molten smelt (sodium carbonate and sodium sulfide) that accumulates on the floor of the furnace is released to the tank where it dissolves in water to form "green liquor." This contact of smelt and water causes large quantities of steam to be released.

From the smelt dissolving tank, the green liquor is pumped to the causticizer where quicklime (CaO) is added to convert the sodium carbonate ($Na_2 CO_3$) to sodium hydroxide ($NaOH$) which is then used as white liquor in the digester process. The causticizer process involves two steps: (1) the reaction of calcium oxide with water to form calcium hydroxide; and (2) the reaction of $CaOH$ with Na_2CO_3 to form $NaOH$ plus a $CaCO_3$ precipitate. The calcium carbonate is then calcined in the lime kiln to produce calcium oxide which is reused in the causticizer process.

The lime kiln is very important in the process. Lime mud from the causticizer is fed to the top of the kiln. The mud is dried by combustion of natural gas or fuel oil in a counter-current flashing. The rotating kiln (1-2 rpm) causes the lime to proceed downward through the kiln towards the high temperature zone (1800-2000°F). As the lime moves down the kiln, it dries and agglomerates into small pellets and finally is calcined to calcium oxide near the exit where the gas/oil fired burner is located. The discharge can either be stored or put directly back into the causticizer.

As can be seen from Figure 2.1, the majority of the process involves recovery of spent chemicals.

2.1.2 Sulfite Process

The sulfite process is very similar to the Kraft pulping process. In the sulfite process, sulfurous acid base solution is used to dissolve the lignin in the wood chips rather than a caustic solution as in the Kraft process. Additional buffering, utilizing bisulfite salts of sodium, calcium, ammonia or magnesium, is required during the cooking in the digester.

The wood chips are cooked in the digester. Then the pressure is reduced and the contents are moved to the blow tank, where the chips are defibered.

The pulp is separated into two groups, the spent liquor and the pulp, through a series of washers. The pulp is then sent to bleaching and finally through the papermaking process.

2.1.3 Neutral Sulfite Semichemical (NSSC)

Two major aspects separate the NSSC process from either the Kraft or sulfite processes. They are:

- The cooking liquor is a neutral solution of sodium sulfite and sodium bicarbonate or sodium carbonate, rather than acidic or basic; and
- Only a portion of the lignin is dissolved in the digester during cooking.

The partially cooked wood chips are further subjected to mechanical attrition to produce the pulp. From this stage, the pulp is bleached and processed similar to the Kraft and sulfite processes to produce paper.

In summary, of the two phases in the production of paper, the pulping of the wood and the manufacture of the paper, the pulping process is the larger source of air pollutants. The Kraft or sulfate pulping process produces over 80 percent of the chemical pulp produced annually in the United States. The remaining 20 percent of the chemical pulp is produced by the sulfite and neutral sulfite semi-chemical (NSSC) processes. Figure 2.2 illustrates the basic process of papermaking. The pulping of wood (utilizing the kraft, sulfite or neutral sulfite semichemical) is solely involved in the digester aspect of papermaking.

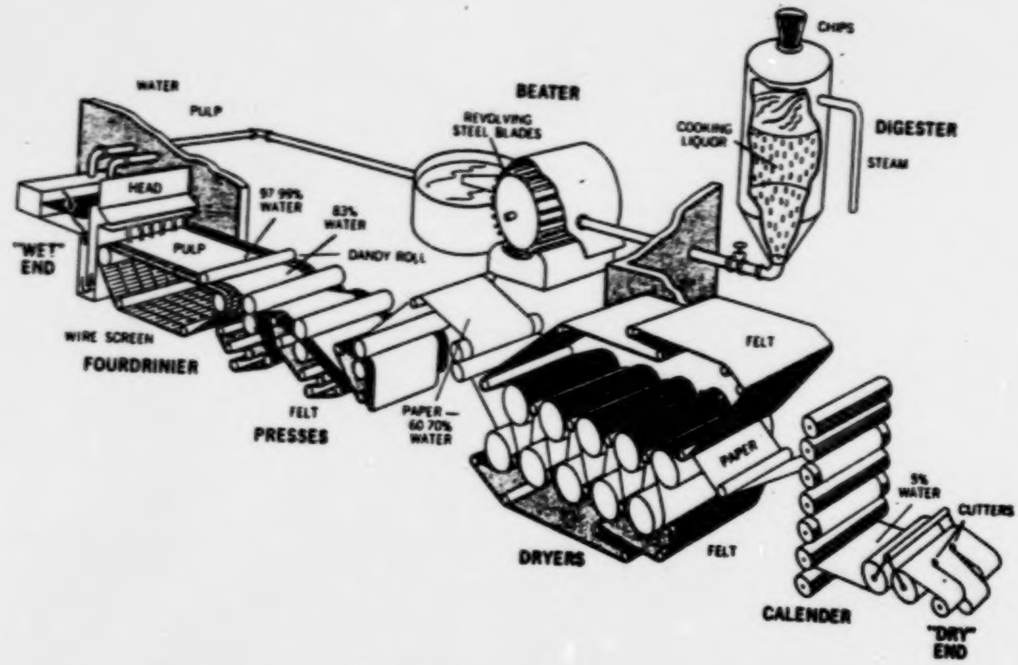
CHIPS
WATER
PULP
BEATER
REVOLVING STEEL BLADES
COOKING LIQUOR
DIGESTER
STEAM
HEAD
97-99% WATER
83% WATER
"WET" END
PULP
DANDY ROLL
WIRE SCREEN
FOURDRINIER
FELT
FELT
PRESSES
PAPER — 60-70% WATER
PAPER
5% WATER
CUTTERS
DRYERS
FELT
CALENDER
"DRY" END

Figure 2.2. Simplified Diagram of the Papermaking Process.

2.2 PULP MILL POPULATION

Since the time the first Kraft mill was built in 1891, the industry has grown to be the 10th largest industrial process in the United States. Table 2.1 reflects the growth of this industry in the production of paper over the last decade.

TABLE 2.1
PULP MILL POPULATION

	Number of Mills		Production, Million Tons	
Process	1968	1984	1968	1984
Kraft	116	126	29.6	42.0
Sulfite	38	26	3.0	1.8
Other[1]	230	237	3.6	3.0
Total	384	389	36.4	46.8

[1] Other includes chemimechanical, alkaline neutral, semi-chemical, cold soda, deinking, rag, rope, flux, bagasse and cotton lintons pulp mills.

Review of Table 2.1 indicates a shift from the sulfite process to the Kraft process over the previous decade.

The names and locations of currently operating pulp mills utilizing the Kraft or sulfite process are listed in Table 2.2.

TABLE 2.2
LOCATION OF PULP MILLS IN THE UNITED STATES

State	Company Name	Location	Process	
			Kraft	Sulfite
Alabama				
	Container Corp. of America	Brewton	X	
	Alabama River Pulp Co.	Claiborne	X	
	Coosa River Newsprint	Coosa Pines	X	
	Champion Paper Corp.	Courtland	X	
	Gulf States Paper Corp.	Demopolis	X	
	Allied Paper, Inc.	Jackson	X	
	Alabama Kraft Co.	Mahrt	X	
	International Paper Co.	Mobile	X	
	Scott Paper Co.	Mobile	X	
	Union Camp Corp.	Montgomery	X	
	James River-Dixie/Northern	Pennington	X	
	MacMillan Bloedel Inc.	Pine Hill	X	
	Hammermill Papers Group	Selma	X	
Alaska				
	Louisiana-Pacific Corp.	Ketchikan		X
	Alaska Pulp Co., Inc.	Sitka		X
Arizona				
	Southwest Forest Industries	Snowflake	X	
Arkansas				
	Nekoosa Papers, Inc.	Ashdown	X	
	International Paper Co.	Camden	X	
	Georgia- Pacific Corp.	Crossett	X	
	Potlatch Corp.	McGehee	X	
	Arkansas Kraft Corp.	Morrilton	X	
	International Paper Co.	Pine Bluff	X	
	Weyerhaeuser Co.	Pine Bluff	X	
California				
	Simpson Paper Co.	Anderson	X	
	Louisiana-Pacific Corp.	Antioch	X	
	Simpson Paper Co.	Fairhaven	X	
	Louisiana-Pacific Corp.	Samoa	X	
Florida				
	St. Regis Corporation	Cantonment	X	
	Container Corp. of America	Fernandina Beach	X	
	ITT Rayonier, Inc.	Fernandina Beach		X
	Alton Packaging Corp.	Jacksonville	X	
	Jacksonville Kraft Paper Co.	Jacksonville	X	
	Georgia-Pacific Corp.	Palatka	X	
	Southwest Forest Industries, Inc.	Panama City	X	
	Buckeye Cellulose Corp.	Foley	X	
	St. Joe Paper Co.	Port St. Joe	X	

TABLE 2.2 (Continued)

State	Company Name	Location	Process	
			Kraft	Sulfite
Georgia				
	Continental Forest Industries	Augusta	X	
	Brunswick Pulp & Paper Co.	Brunswick	X	
	Great Southern Paper Co.	Cedar Springs	X	
	ITT Rayonier, Inc.	Jesup	X	
	Georgia Kraft Co.	Krannert	X	
	Georgia Kraft Co.	Macon	X	
	Buckeye Cellulose Corp.	Oglethorpe	X	
	Stone Container Corp.	Port Wentworth	X	
	Interstate Paper Corp.	Riceboro	X	
	Gilman Paper Co.	Saint Marys	X	
	Union Camp Corp.	Savannah	X	
	Owens-Illinois Inc.	Valdosta	X	
Idaho				
	Potlatch Corp.	Lewiston	X	
Kentucky				
	Willamette Industries Inc.	Hawesville	X	
	Westvaco Corp.	Wickliffe	X	
Louisiana				
	International Paper Co.	Bastrop	X	
	Crown Zellerbach Corp.	Bogalusa	X	
	Willamette Industries	Campti	X	
	Boise Southern Co.	De Ridder	X	
	Boise Southern Co.	Elizabeth	X	
	Stone Container Corp.	Hodge	X	
	International Paper Co.	Mansfield	X	
	International Paper Co.	Pineville	X	
	Georgia-Pacific Corp.	Port Hudson	X	
	International Paper Co.	Springhill	X	
	Manville Forest Products Corp.	West Monroe	X	
Maine				
	Statler Tissue Co.	Augusta		X
	Scott Paper Co.	Hinckley	X	
	International Paper Co.	Jay	X	
	Lincoln Pulp & Paper Co., Inc.	Lincoln	X	
	Great Northern Paper Co.	Millinocket		X
	James River Corporation	Old Town	X	
	Boise Cascade Corp.	Rumford	X	
	S. D. Warren Co.	Westbrook	X	
	Georgia-Pacific Corp.	Woodland	X	
	Scott Paper Company	Winslow		X

TABLE 2.2 (Continued)

State	Company Name	Location	Process	
			Kraft	Sulfite
Maryland				
	Westvaco Corp.	Luke	X	
Michigan				
	Mead Corp.	Escanaba	X	
	S. D. Warren Co.	Muskegon	X	
Minnesota				
	Potlatch Corp.	Cloquet	X	
	Boise Cascade Corp.	International Falls	X	
Mississippi				
	Georgia Pacific Corp.	Monticello	X	
	International Paper Co.	Moss Point	X	
	International Paper Co.	Natchez	X	
	International Paper Co.	Vicksburg	X	
	Leaf River Forest Products, Inc.	New Augusta	X	
Montana				
	Champion Packaging Corp.	Missoula	X	
New Hampshire				
	James River Corp.	Berlin	X	
New York				
	Finch, Pruyn & Co., Inc.	Glens Falls		X
	International Paper Co.	Ticonderoga	X	
North Carolina				
	Champion Paper Corp.	Canton	X	
	Weyerhaeuser Co.	New Bern	X	
	Olin Corp.	Pisgah Forest	X	
	Weyerhaeuser Co.	Plymouth	X	
	Federal Paper Board Co.	Riegelwood	X	
	Champion Packaging Corp.	Roanoke Rapids	X	
Ohio				
	Mead Corp.	Chillicothe	X	
Oklahoma				
	Weyerhaeuser Co.	Valliant	X	
Oregon				
	Willamette Industries Inc.	Albany	X	
	Crown Zellerbach Corp.	Clatskanie	X	
	International Paper Co.	Gardiner	X	
	James River-Dixie/Northern	Halsey	X	
	Crown Zellerbach Corp.	Lebanon		X
	Publishers Paper Co.	Newberg		X
	Publishers Paper Co.	Oregon City		X
	Boise Cascade Corp.	Salem		X
	Weyerhaeuser Co.	Springfield	X	
	Georgia-Pacific Corp.	Toledo	X	
	Boise Cascade Corp.	St. Helens	X	

TABLE 2.2 (Continued)

State	Company Name	Location	Process	
			Kraft	Sulfite
Pennsylvania				
	Penntech Papers Inc.	Johnsonburg	X	
	Appleton Papers, Inc.	Roaring Spring	X	
	P. H. Glatfelter Co.	Spring Grove	X	
South Carolina				
	Bowaters Carolina Co.	Catawba	X	
	Union Camp Corp.	Eastover	X	
	Stone Container Corp.	Florence	X	
	International Paper Co.	Georgetown	X	
	Westvaco Corp.	North Charleston	X	
Tennessee				
	Bowater Southern Paper Corp.	Calhoun	X	
	Tennessee River Pulp & Paper Co.	Counce	X	
Texas				
	St. Regis Corp.	Houston	X	
	St. Regis Corp.	Lufkin	X	
	Owens-Illinois, Inc.	Orange	X	
	Champion Paper Corp.	Pasadena	X	
	International Paper Co.	Texarkana	X	
	Temple-Eastex Inc.	Silsbee	X	
Virginia				
	Westvaco Corp.	Covington	X	
	Union Camp Corp.	Franklin	X	
	Stone Container Corp.	Hopewell	X	
	Chesapeake Corp. of Virginia Inc.	West Point	X	
Washington				
	Georgia-Pacific Corp.	Bellingham		X
	Crown Zellerbach Corp.	Camas	X	
	Weyerhaeuser Co.	Cosmopolis		X
	Scott Paper Co.	Everett		X
	Longview Fiber Co.	Longview	X	
	Weyerhaeuser Co.	Longview	X	
	Crown Zellerbach Corp.	Port Townsend	X	
	St. Regis Paper Co.	Tacoma	X	
	Boise Cascade Corp.	Wallula	X	
	Scott Paper Co.	Anacortes		X
	Weyerhaeuser Co.	Everett	X	
	ITT Rayonier Inc.	Hoquiam		X
*	ITT Rayonier Inc.	Port Angeles		X

TABLE 2.2 (Continued)

State / Company Name	Location	Process: Kraft	Process: Sulfite
Wisconsin			
Consolidated Papers, Inc.	Appleton		X
Wausau Paper Mills Co.	Brokaw		X
James River-Dixie/Northern	Green Bay		X
Procter & Gamble Paper Products Co.	Green Bay		X
Thilmany Pulp & Paper Co.	Kaukauna	X	
Mosinee Paper Corp	Mosinee	X	
Nekoosa Papers Inc.	Nekoosa	X	
Badger Paper Mills, Inc.	Peshtigo	X	
Nekoosa Papers, Inc.	Port Edwards		X
Rhinelander Paper Co. Inc.	Rhinelander		X
Weyerhaeuser Co.	Rothschild		X
Consolidated Papers, Inc.	Wisconsin Rapids	X	
Scott Paper Co.	Oconto Falls		X
Flambeau Paper Co.	Park Falls		X

Table 2.3 summarizes the total number of pulp mills within each state. Major emissions of total reduced sulfur (TRS) occur from the Kraft process, while sulfur dioxide (SO_2) emissions are predominant from the sulfite process. Other process (de-inking, defibrated wood, etc.) have minimum emissions.

TABLE 2.3
PULP MILL POPULATION PER STATE

State[3]	Pulp Mills (Total)[1]	Pulp Mill Process: Kraft	Pulp Mill Process: Sulfite	Pulp Mill Process: Other[2]
Alabama	23	13	-	10
Alaska	2	-	2	-
Arizona	5	1	-	4
Arkansas	9	7	-	2
California	14	4	-	10
Connecticut	2	-	-	2
Delaware	1	-	-	1
Florida	11	8	1	2
Georgia	22	12	-	10
Idaho	1	1	-	-
Illinois	4	-	-	4
Indiana	2	-	-	2
Iowa	2	-	-	2
Kentucky	3	2	-	1
Louisiana	21	11	-	10
Maine	23	7	3	13
Maryland	2	1	-	1
Massachusetts	7	-	-	7
Michigan	12	2	-	10
Minnesota	11	2	-	9
Mississippi	10	5	-	5

Contd.

TABLE 2.3 (Contd.)
PULP MILL POPULATION PER STATE

State[3]	Pulp Mills (Total)[1]	Pulp Mill Process		
		Kraft	Sulfite	Other[2]
Missouri	1	-	-	1
Montana	1	1	-	-
New Hampshire	4	1	-	3
New Jersey	5	-	-	5
New York	17	1	1	15
North Carolina	12	6	-	6
Ohio	11	1	-	10
Oklahoma	6	1	-	5
Oregon	26	7	4	15
Pennsylvania	9	3	-	6
Puerto Rico	1	-	-	1
South Carolina	12	5	-	7
Tennessee	13	2	-	11
Texas	11	6	-	5
Vermont	2	-	-	2
Virginia	11	4	-	7
Washington	23	7	6	10
Wisconsin	37	5	9	23
TOTAL	389	126	26	237

[1] Total includes Kraft, sulfite, NSSC, de-inked, defibrated wood, ground, rags, etc., pulp processing mills.

[2] Includes chem-mechanical, alkaline neutral, semi-chemical, cold soda, rag, rope, flax, bagasse and cotton linters pulp mills.

[3] States not listed have no pulp mills (Kansas, Connecticut, New Mexico, Colorado, Nebraka, Rhode Island, West Virginia, North Dakota, South Dakota, Wyoming, Utah, Nevada and Hawaii).

Table 2.4 summarizes the number of pulp mills located within each state while Table 2.5 lists number of pulp mills per Region.

TABLE 2.4
STATE LOCATION OF PULP MILLS

Location	Pulp Mills		Kraft Mills	
	Total	% of Total	Total	% of Total
Region I				
o Maine	23	5.9	7	5.6
o New Hampshire	4	1.0	1	0.8
o Vermont	2	0.5	-	0.0
o Connecticut	2	0.5	-	0.0
o Massachusetts	7	1.8	-	0.0
o Rhode Island	-	0.0	-	0.0
Region II				
o N.Y.	17	4.4	1	0.8
o N.J.	5	1.3	-	0.0
o Puerto Rico	1	0.3	-	0.0
o Virgin Islands	0	0.0	-	0.0
Region III				
o Pennsylvania	9	2.3	3	2.4
o Maryland	2	0.5	1	0.8
o Virginia	11	2.8	4	3.2
o West Virginia	-	0.0	-	0.0
o Delaware	1	0.3	-	0.0
o District of Columbia	0	0.0	-	0.0
Region IV				
o N.C.	12	3.1	6	4.8
o S.C.	12	3.1	5	4.0
o Georgia	22	5.7	12	9.5
o Alaska	23	5.9	13	10.3
o Mississippi	10	2.6	5	4.0
o Florida	11	2.8	8	6.3
o Tennessee	13	3.3	2	1.6
o Kentucky	3	0.8	2	1.6
Region V				
o Ohio	11	2.8	1	0.8
o Indiana	2	0.5	-	0.0
o Illinois	4	1.0	-	0.0
o Wisconsin	37	9.5	5	4.0
o Minnesota	11	2.8	2	1.6
o Michigan	12	3.1	2	1.6
Region VI				
o Texas	11	2.8	6	4.8
o Oklahoma	6	1.5	1	0.8
o Arkansas	9	2.3	7	5.6
o Louisiana	21	5.4	11	8.7
o New Mexico	-	0.0	-	0.0

TABLE 2.4 (Continued)
STATE LOCATION OF PULP MILLS

Location	Pulp Mills		Kraft Mills	
	Total	% of Total	Total	% of Total
Region VII				
o Kansas	-	0.0	-	0.0
o Nebraska	-	0.0	-	0.0
o Iowa	2	0.5	-	0.0
o Missouri	1	0.3	-	0.0
Region VIII				
o Colorado	-	0.0	-	0.0
o North Dakota	-	0.0	-	0.0
o South Dakota	-	0.0	-	0.0
o Montana	1	0.3	1	0.8
o Wyoming	-	0.0	-	0.0
o Utah	-	0.0	-	0.0
Region IX				
o California	14	3.6	4	3.2
o Nevada	-	0.0	-	0.0
o Hawaii	-	0.0	-	0.0
o Arizona	5	1.3	1	0.8
o American Samoa	0	0.0	-	0.0
o Guam	0	0.0	-	0.0
Region X				
o Washington	23	5.9	7	5.6
o Oregon	26	6.7	7	5.6
o Idaho	1	0.3	1	0.8
o Alaska	2	0.5	-	0.0

TABLE 2.5
REGIONAL LOCATION OF PULP MILLS

U. S. EPA Region	Pulp Mills		Kraft Mills	
	Total	% of Total	Total	% of Total
I	38	9.8	8	6.3
II	23	5.9	1	0.8
III	23	5.9	8	6.3
IV	106	27.2	53	42.1
V	77	19.8	10	7.9
VI	47	12.1	25	19.8
VII	3	0.8	0	0.0
VIII	1	0.3	1	0.8
IX	19	4.9	5	4.0
X	52	13.4	15	11.9

2.3 KRAFT PULP MILL EMISSIONS

While other industries, such as the petroleum industry, photochemical plant complexes, coke oven plants, dye manufacturers and others have odorant problems, the Kraft paper mill industry has made more people aware of its presence due to its characteristic odors. The pulp and paper manufacturing is reported to be the tenth largest manufacturing industry in the United States, accounting for nearly 4 percent of the value of all manufacturing. As indicated earlier, it consists of two well defined segments: pulping and paper making. Pulping is the conversion of fibrous raw materials such as wood, cotton, or used paper into a material suitable for use in paper, paperboard, and building material. Wood is the dominant source of fibers for paper production. As discussed earlier pulp is produced by two general methods: (1) mechanical pulp is produced by grinding or shredding the wood to free the fibers; and (2) chemical pulp is produced by cooking wood chips in chemical solutions that dissolve the lignin binding material. Air pollution emissions of the chemical pulping processes are more significant than those of the mechanical processes.

Within the chemical pulping process, numerous sources of both gaseous and particulate matter emissions occur. The gaseous emissions are principally hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide and sulfur dioxide. Because the process involves chemical digestion, washing and stripping to produce the pulp and because the solutions used within the industry are some form of sulfur, the emissions occur throughout the process. They are all extremely odorous and are detectable at concentrations as low as 1 part per billion (ppb). Figure 2.3 illustrates major emission points within the Kraft pulp mill and Table 2.5 reflects typical emission from those sources.

2.3.1 Components of Kraft Pulp Mill Odor

Hydrogen sulfide (H_2S) is the most important of the four odorants. Of the TRS (total reduced sulfur) emissions, it is the most common and the most researched.

Hydrogen sulfide emissions originate from the breakdown of sodium sulfide, a component of the Kraft cooking liquor. Essentially, it is a weak acidic gas which partially ionizes in the water-based Kraft cooking liquor. The ionization occurs in two stages: (1) the forming of hydrosulfide; and (2) with increasing pH, the sulfide ion forms, as indicated by the following equation:

$$H_2S \longrightarrow HS^- + H^+ \longrightarrow S^= + 2H^+$$

The black liquor in the Kraft pulping process contains a high concentration of dissolved sodium sulfide in a strongly alkaline solution. If the pH were lowered, the sodium sulfide would hydrolyze to sodium hydrosulfide. Below pH 8, some unionized hydrogen sulfide would form as the reaction equilibrium in the above equation moves from the right side to the left side. At a pH of about 8.0, most hydrogen sulfide forms hydrosulfide ions. As a result, in the Kraft pulping process, there is usually very small amounts of hydrogen sulfide in the liquor. It is almost always present in larger amount than the mercaptans or other sulfur compounds. When H_2S is present, other sulfur emissions may be, but if it is not present, other sulfur emissions are unlikely.

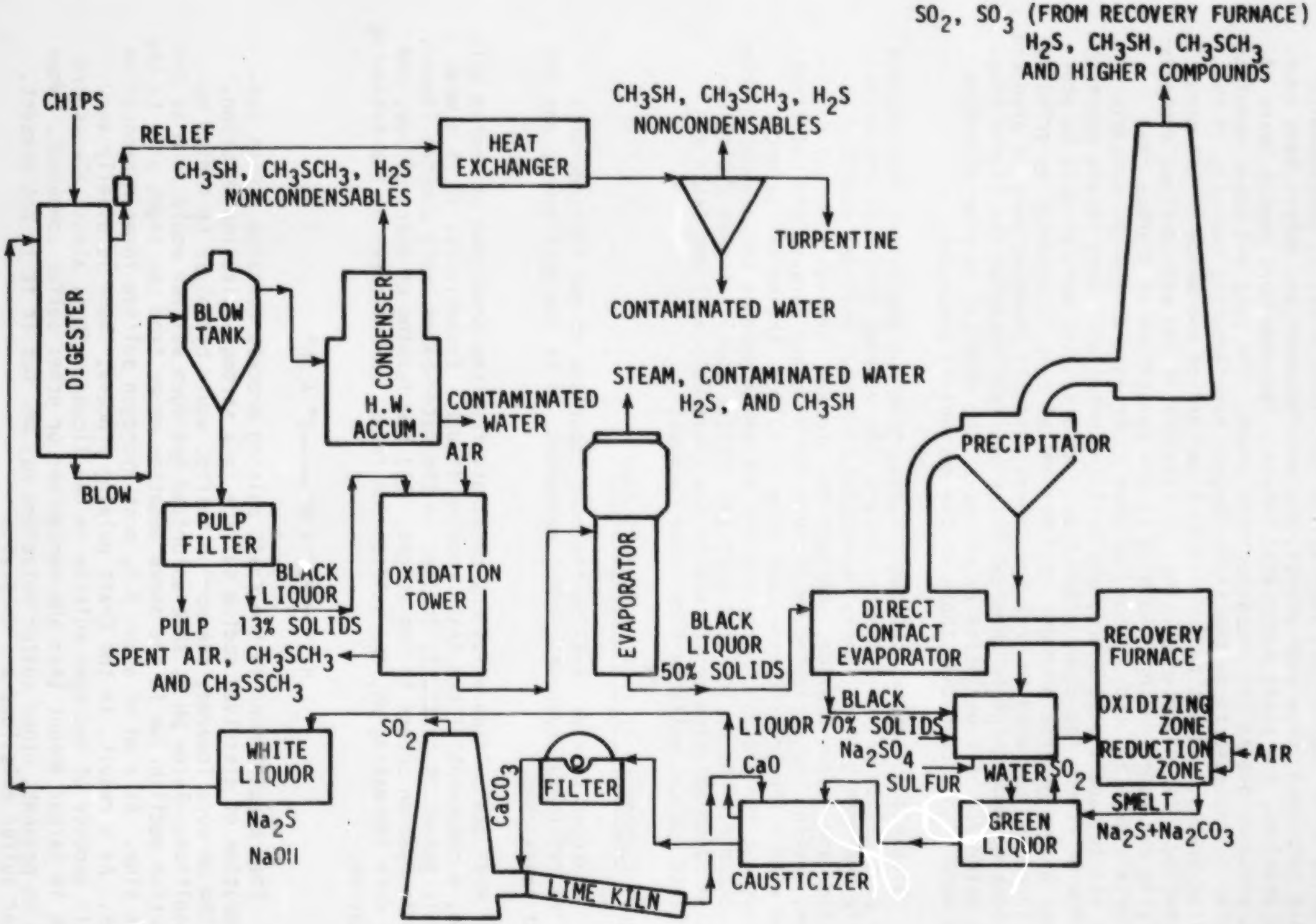
SO$_2$, SO$_3$ (FROM RECOVERY FURNACE)
H$_2$S, CH$_3$SH, CH$_3$SCH$_3$
AND HIGHER COMPOUNDS
CHIPS
RELIEF
HEAT EXCHANGER
CH$_3$SH, CH$_3$SCH$_3$, H$_2$S
NONCONDENSABLES
CH$_3$SH, CH$_3$SCH$_3$, H$_2$S
NONCONDENSABLES
TURPENTINE
CONTAMINATED WATER
DIGESTER
BLOW TANK
CONDENSER
H.W. ACCUM.
CONTAMINATED WATER
STEAM, CONTAMINATED WATER
H$_2$S, AND CH$_3$SH
PRECIPITATOR
BLOW
PULP FILTER
AIR
OXIDATION TOWER
EVAPORATOR
BLACK LIQUOR
PULP
13% SOLIDS
SPENT AIR, CH$_3$SCH$_3$
AND CH$_3$SSCH$_3$
BLACK LIQUOR
50% SOLIDS
DIRECT CONTACT EVAPORATOR
RECOVERY FURNACE
OXIDIZING ZONE
REDUCTION ZONE
AIR
BLACK
LIQUOR 70% SOLIDS
Na$_2$SO$_4$
SULFUR
WATER
SO$_2$
SMELT
Na$_2$S+Na$_2$CO$_3$
GREEN LIQUOR
CaO
CAUSTICIZER
SO$_2$
CaCO$_3$
FILTER
LIME KILN
WHITE LIQUOR
Na$_2$S
NaOH

Figure 2.3. Major Emission Points Within The Kraft Pulp Mill

TABLE 2.6
TYPICAL EMISSIONS CONCENTRATIONS FOR SULFUR COMPOUNDS FROM KRAFT PULP MILLS

Emission Source	Pollutants Concentration ppm by Volume				
	Sulfur Dioxide SO_2	Hydrogen Sulfide H_2S	Methyl Mercaptan CH_3SH	Dimethyl Sulfide $(CH_3)_2S$	Dimethyl Disulfide $(CH_3)_2S_2$
Recovery Furnace No auxiliary fuel	0-1200	0-1500	0-200	0-100	2-95
Auxiliary fuel added	0-1500	0-1500	0-200	0-100	2-95
Smelter Dissolving Tank	0-100	0-75	0-2	0-4	0-3
Lime Kiln	0-200	0-250	0-100	0-50	0-20
Digester, brown stock Washer, evaperation, oxidation tower or stripper system	0-100	0-1,000	0-10,000	100-45,000	10-10,000

The hydrogen sulfide that does exist is formed in the recovery furnace and the lime kiln, as that is where the sulfur-containing compounds from the black liquor or lime mud are volatilized and reduced.

Methyl mercaptan (CH_3SH) is a reduced sulfur compound which is formed during the Kraft cook by the reaction of hydrosulfide ion and the methoxy-lignin component of the wood as illustrated in the following equation:

$$\text{Lignin} -OCH_3 + HS^- \rightarrow CH_3SH + \text{Lignin} - O^-$$

Methyl mercaptan will also breakdown in a water-based solution to methyl mercaptan ion. It is reported that this dissociation is essentially complete above a pH of 12.0. Methyl mercaptan is, therefore, present in low concentrations as a dissolved gas in the black liquor. As the pH decreases, additional CH_3SH gas is evolved.

Methyl mercaptan is primarily emitted from the digester relief valve during pressure release, and from the brown stock washers where the pH of the liquor drops below the equilibrium point. Emissions decrease as the residual concentration in the liquor diminishes.

Dimethyl Sulfide $(CH_3)_2S$ is primarily formed through the reaction of mercaptide ion with the methoxy-lignin component of the wood:

$$\text{Lignin} - OCH_3 + CH_3S \rightarrow \text{Lignin} - O^- + (CH_3)_2S$$

Dimethyl sulfide may also be formed by the disproportionation of methyl mercaptan. At normal liquor temperature (150-200°F) it is highly volatile. It does not, however, dissociate as hydrogen sulfide and methyl mercaptan do.

Dimethyl disulfide $(CH_3)_2S_2$ is formed by the oxidation of methyl mercaptan throughout the recovery system, especially in the oxidation towers, by the following equation:

$$4\ CH_3SH + O_2 \rightarrow 2\ (CH_3)_2S_2 + 2\ H_2O$$

Dimethyl disulfide has a higher boiling point than any of the other compounds and its retention in the liquor is therefore greater.

2.3.2 Effects

2.3.2.1 Human - The human effects of these compounds vary depending upon concentration and depending upon the individual. While reactions to these odors are fairly subjective, researchers agree that at sufficiently high concentrations, the compounds are very toxic to humans.

For example, hydrogen sulfide acts as a cell and enzyme poison and can cause irreversible changes on nerve tissue. It enters the body through the respiratory tract, and then is transferred by the blood stream to various body organs. When hydrogen sulfide enters the blood, it can lead to a blockage of oxygen transfer, especially at higher concentrations.

Some of the effects of hydrogen sulfide and the air concentrations at which they occur are shown in Table 2.7.

TABLE 2.7
EFFECTS OF HYDROGEN SULFIDE INHALATION ON HUMANS

Hydrogen Sulfide µg/m^3 (ppm)	Effects
1-45 (7.2×10^{-4} - 3.2×10^{-2})	Odor threshold. No reported injury to health
10 (7.2×10^{-3})	Threshold of reflex effect on eye sensitivity to light
150 (0.10)	Smell slightly perceptible
500 (0.40)	Smell definitely perceptible
15,000 (10.0)	Minimum concentration causing eye irritation
30,000 (20.0)	Maximum allowable occupational exposure for 8 hours (ACGIH Tolerance Limit)
30,000-60,000 (20.0-40.0)	Strongly perceptible but not intolerable smell. Minimum concentration causing lung irritation
150,000 (110)	Olfactory fatigue in 2-15 minutes; irritation of eyes and respiratory tract after 1 hour; death in 8 to 48 hrs.
270,000-480,000 (200-350)	No serious damage for 1 hour but intense local irritation; eye irritation in 6 to 8 minutes
640,000-1,120,000 (460-810)	Dangerous concentration after 30 minutes or less
900,000 (650)	Fatal in 30 minutes
1,160,000-1,370,000 (840-990)	Rapid unconsciousness, respiration arrest, and death, possibly without odor sensation
1,500,000+ (1100+)	Immediate unconsciousness and rapid death

At concentrations over 1,120,000 $\mu g/m^3$ there is practically no sensation of smell due to olfactory fatigue and death can occur quickly. Loss of sense of smell has even been reported at concentrations of 150,000 $\mu g/m^3$ after exposure time of 2 to 15 minutes.

Concentrations in and around Kraft paper mills are a lot less than the figures mentioned above. While the Occupational Safety and Health Administration (OSHA) has established a maximum allowable exposure concentration for hydrogen sulfide of 30,000 $\mu g/m^3$ and 15,000 $\mu g/m^3$ for methyl mercaptans, concentrations are usually a lot lower.

At lower concentrations human response to hydrogen sulfide varies considerably among individuals depending upon the age and sex of the individuals, the size of the town in which they live, and whether they smoke. For example, the odor threshold of hydrogen sulfide varies between 1 and 45 $\mu g/m^3$.

Concentrations of TRS as high as 30,000 $\mu g/m^3$ (20 ppm) are not likely to be realized near existing Kraft pulp mills. For example, measurements of ambient hydrogen sulfide concentration were made during a six-month period in 1961 and 1962 in the Lewiston, Idaho area where the major contributor of gaseous pollutants was a pulp mill which had only the recovery furnace controlled for TRS emissions. The levels of hydrogen sulfide were generally less than 15 $\mu g/m^3$. During an air pollution episode in November 1961, peak 2-hour concentrations of 77 $\mu g/m^3$ were measured. These levels are well below the maximum allowable occupational exposure concentration established by OSHA.

Some common physical complaints include: metallic taste, fatigue, diarrhea, blurred vision, intense aching of the eyes, insomnia, and vertigo. Emotional reactions to malodorous compounds such as hydrogen sulfide have also been noted to produce physical responses: headache, feelings of nausea, vomiting, decrease in appetite, impairing nutrition and water intake, hampering proper breathing, offending the senses. Most of all, malodors can upset good dispositions, provoke emotional disturbances, mental depression and irritability.

2.3.2.2 Sociological - From a sociological standpoint, foul odors can ruin personal and community pride, interfere with human relations in various ways, discourage capital improvements, lower socioeconomic status, and damage a community's reputation.

Communities are also affected physically. Some compounds, such as hydrogen sulfide react with paints containing heavy metal salts to darken or discolor a surface. Likewise, copper and silver tarnish quickly in the presence of hydrogen sulfide.

2.3.2.3 Vegetation - Hydrogen sulfide emissions can also be harmful to vegetation. Table 2.7 indicates the time until 50 percent injury to various vegetation exposed to 1,500,000 $\mu g/m^3$ of hydrogen sulfide. Though injury occurs to vegetation at high concentrations, there is little evidence to support this claim at lower levels. Experimentation revealed that little or no injury occurred to 29 species of plants when they were sprayed with less than 60,000 $\mu g/m^3$ of hydrogen sulfide for five hours.

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After five hours at 600,000 μg/m^3, some species were injured, but not all. Boston fern, apple, cherry, peach and coleus showed appreciable injury at concentrations of 600,000 μg/m^3. At concentrations between 60,000 and 600,000 μg/m^3, gladiolus, rose, castor bean, sunflower, and buckwheat showed moderate injury. Tobacco, cucumber, salvia, and tomato were slightly more sensitive.

In general, hydrogen sulfide injures the youngest plant leaves rather than the middle-aged or older ones. Young, rapidly elongating tissues are the most severely injured. Typical exterior symptoms are wilting without typical discoloration (which starts at the tip of the leaf). The scorching of the youngest leaves of the plant occurs first.

TABLE 2.8
TIME IN MINUTES UNTIL 50 PERCENT INJURY TO EXPOSED PLANT SURFACES AT 1,500,000 μg/m^3 HYDROGEN SULFIDE

Plant Surface	Plant	Time in Minutes
Leaves	Tomato	30
	Buckwheat	60
	Tobacco	100
Stems	Tomato	45
	Buckwheat	120
	Tobacco	480

2.3.2.4 Economic - There are also economic repercussions. Malodorous compounds can stifle growth and the development of a community. Both industry and workers tend to locate in an area which is desirable to live, work, recreate and the natural tendency is to avoid cities and towns with obvious odor problems. Tourists also avoid such areas. Communities with an odor problem often experience a decline in property values, tax revenues, payrolls, and sales. This can be an economic disaster to the community.

2.4 LIMITING EMISSIONS

Movement towards doing something about the emission problems from Kraft pulp mills began in the 1960's, when it was realized how harmful these emissions can be and when it was realized that chemical pulp production was going to double between 1970 and 1985, rising by about 35 million to 70 million tons annually. Most of this production is produced by the Kraft process.

Residents of several communities, Eureka, California, among them, began to organize to combat the problem. In 1967, at their 29th Annual Meeting, the American Conference of Governmental Industrial Hygienists (ACGIH), set the workplace threshold limit for hydrogen sulfide in air for an eight-hour-day, 40-hour week at 15,000 $\mu g/m^3$. The hydrogen sulfide ambient air quality standards for various states and governments are shown in Table 2.9.

TABLE 2.9
HYDROGEN SULFIDE AMBIENT AIR QUALITY STANDARDS

Country or State	Basic Standard		Maximum Single Measurement
	$\mu g/m^3$	Avg. Time	$\mu g/m^3$
California	150	1 hr	
Missouri	45	30 min	
Montana	45	30 min	
New York	150	1 hr	
Pennsylvania	7.5	24 hr	
Texas	120	30 min	
Czechoslovokia	8	24 hr	8
Canada (Ontario)	45	30 min	
Poland	20	24 hr	
U.S.S.R	8	24 hr	8
Federal Republic of Germany	150	30 min	

In 1970, the Clean Air Act required all states to prepare a state implementation plan (SIP) that set forth how the State intended to attain and maintain the National Ambient Air Quality Standards (NAAQS). Each SIP must contain among other things the necessary legal authority and emission limitations to ensure attainment and maintenance of the NAAQS.

The Clean Air Act of 1970 and the initial SIPs developed under that Act placed primary emphasis on initial compliance of sources with a set of specified emission limitations that reduced emissions sufficiently to attain the NAAQS. Less attention and consideration were initially given in the formulation of control strategies that would preserve or maintain the air quality once attainment was achieved.

In addition, EPA has worked with state governments in establishing specific TRS compliance deadlines. By June 1982, the digester and evaporation tanks of Kraft pulp mills were controlled within EPA standards. The established compliance deadlines were April, 1984, for lime kilns and December, 1984 for recovery boilers.

Control agencies have long recognized that initial compliance does not necessarily mean future or continuing compliance. Faced with limited resources, attainment dates mandated by legislation, emission limits set by regulations, and already established source compliance dates, the agencies understandably placed a greater emphasis on promoting initial source compliance to ensure attainment of NAAQS. Now that most sources have either demonstrated initial compliance or are in the midst of a compliance-oriented program, considerable concern has been raised within the air pollution control community with respect to whether a source is operating and maintaining its control equipment. Some concern has also been raised with respect to whether a source is complying with the applicable emission limit on a continuous basis. In many cases, a source can fine tune its control system and make the necessary adjustments to comply with an emission limit during a stack test conducted to certify compliance with the applicable emission limit. Once these tests have been completed, however, the control system may begin to deteriorate and the source may no longer be in compliance with the applicable emission limit.

Consequently, in the last few years, continuous emission monitors have become more prevalent as a means of ensuring continuous compliance with emission limitations established for stationary sources. Standards of performance established by the EPA for new sources presently require the use of continuous emission monitors (CEM) on many industrial sources. Other new industrial sources will be required to install and operate CEMs when performance specifications are promulgated by EPA. The application of continuous emission monitoring on Kraft pulp mills is just one example of EPA's efforts to ensure continuous compliance of regulated facilities.

2.5 SUMMARY

In summary, over 80% of wood pulp produced in the United States is by the Kraft process, the major source of TRS emissions. Characteristic emissions of the pulp industry coupled with its status as the 10th largest industry in the U. S. has caused establishment of hydrogen sulfide ambient air quality standards in many states and emission limitation on NSPS Kraft pulp mills.

3.0 REGULATIONS

3.1 THE CLEAN AIR ACT AND ITS AMENDMENTS

Regulatory authority associated with the enforcement of air quality standards has its basis in the Clean Air Act and its amendments. More importantly, the Clean Air Act Amendments of 1970 established the Environmental Protection Agency, which was given the mandate to set and enforce the regulations. It became the responsibility of EPA to "protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population..." In essence, EPA was mandated to protect the public health and welfare of its citizens. To accomplish this, EPA established national ambient air quality standards (NAAQS) for major air pollutants. The 1970 Amendments established dates for attaining the ambient standards. Section 110 of the Act required all states to submit a State Implementation Plan (SIP) describing the legislative and regulatory process by which the state was going to attain and maintain NAAQS by the statutory date. The SIP would be formulated by the state and approved by EPA. This created a cooperative state - federal partnership as a means of implementing the Act. EPA sets the standards while the states achieve and maintain those standards. In contrast to the 1967 legislation, the new Act provided the framework for enforcing its provisions. The Clean Air Act of 1963 was part of a series of legislation passed by Congress to protect the environment. Those major pieces of legislation are:

- 1963 - Clean Air Act (P.L. 88-207)

  It was not until 1963 that meaningful legislation in air pollution occurred. The Clean Air Act of 1963 enabled the federal government, at the request of the state, to conduct public hearings on industrial polluters within that state and if necessary, request federal court action.

- 1967 - Air Quality Act (P.L. No. 90-148)

  The fundamental basis of the Air Quality Act of 1967, as amended in 1970 and in 1977, was that major responsibility for control of air pollution from stationary sources rested with state and local programs. EPA may get in the picture only in the event that state or local programs fail to enforce the legislation.

- 1969 - National Environmental Policy Act (P.L. No. 91-190)

  The National Environmental Policy Act (NEPA) introduced the concept of preconstruction review in the form of the Environmental Impact Statement (EIS). The EIS required that the environmental effects of an industrial project must be examined at the conception of the project.

NEPA established a national policy for the environment, and was followed by an explosion of federal enactments such as the Clean Air Act Amendments of 1970 and the 1972 Amendments to the Federal Water Pollution Control Act along with their associated regulations including permit systems and preconstruction (or "new source") review.

- 1970 - Clean Air Act Amendments (P.L. No. 91-704)
- 1977 - Clean Air Act Amendments (P.L. No. 95-95)

Present day enforcement activities are based on the 1977 Clean Air Act Amendments. Those sections of the 1977 Act dealing with Federal Enforcement actions are:

- Section 112: National Emission Standards for Hazardous Air Pollutants (NESHAPS)

  Section 112 of the Act requires the Administrator of EPA to establish standards for air pollutants to which no ambient air quality standard is applicable and which in the judgment of the Administrator may cause, or contribute to "an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness." A NESHAP standard applies to any new or modified source. In addition, existing sources are required to comply with a NESHAP standard within ninety days after its effective date.

- Section 113: SIP Violations

  This section provides that whenever the EPA Administrator finds that a violation of a SIP requirement is occurring, he shall notify the person who is violating the plan and the state in which the plan applies. If such violation extends beyond the thirtieth day after notification, the Administrator may issue an order requiring the violator to comply with the requirements of the SIP or he may bring civil action in court for appropriate relief, including a permanent or temporary injunction, and/or a civil penalty or not more than $25,000 per day of violation.

Under the Clean Air Act of 1970, states were required as part of their SIP, to establish a permit system for preconstruction review of stationary sources. Guidelines were broad, with little or no specific direction. In contrast, the 1977 Amendments set forth detailed review requirements that must be performed prior to the issuance of the permit. Basically, the following standards must be met:

- Section 111: New Source Performance Standards (NSPS)

  Section 111 of the Act requires the Administrator to publish a list of categories of stationary sources which may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare. He must then propose regulations establishing standards of performance for new sources within each category. Enforcement of these standards can be delegated to the states.

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- Section 160-169: Prevention of Significant Deterioration (PSD)

  The basic PSD requirement as set out in Section 165 of the Act provides that no major emitting facility (as defined in the Act) for which construction is commenced after August 7, 1977, may be constructed unless:

  a. A permit has been issued setting forth emission limitation;
  b. An air quality sampling analysis has been conducted;
  c. Certain specified increments are not exceeded;
  d. Best available control technology (BACT) is applied:
  e. The requirements for protection of pristine areas (class 1) have been met;
  f. There has been an analysis of any air quality impacts projected for the area as a result of growth associated with the proposed facility; and
  g. Monitoring will be conducted to determine the effect of the facility's emissions on air quality.

The basic concept of PSD was that EPA, with assistance from the state, should preserve those areas of the country with air quality cleaner than that prescribed by the NAAQS. A source, if located in one of those areas, would have to meet the permit review requirements as stated above.

One of the most interesting changes in the concept of PSD is that it originally applied only in areas that were "cleaner" than the NAAQS. However, the regulations now extend the PSD preconstruction review to any "major emitting facility" no matter where that facility will be located. The rationale behind the expansion is that a source located in a nonattainment area might affect the air quality in a clean area.

- Section 171-178: Nonattainment Areas

  The 1970 version of the Act set 1977 as the date by which all areas had to meet the NAAQS. Many areas of the country, however, failed to meet that date. Consequently, these nonattainment areas force states to revise their SIPs to ensure attainment and maintenance of the standards. EPA developed regulations on emission "tradeoff" or "offset" as an interim policy. The interim policy provides that major sources are subject to an air quality analysis and if the allowable emissions from the proposed source exceeds the NAAQS, approval may be granted only if the source achieves lowest achievable emission rate (LAER), or complies with State SIP or makes reasonable further progress (RFP) toward attainment of the applicable NAAQS.

3.2 CONTINUOUS EMISSION MONITORING BASIS IN THE CLEAN AIR ACT

The Clean Air Act and its amendments is the nation's Federal Law designed to protect the health and welfare of the nation's population. To protect the health and welfare of the nation's population, the Act provided three basic programs regulating emissions from stationary sources:

- SIP requirements for new and existing sources as necessary to attain and maintain the national ambient air quality standards, including new source permitting requirements;

Technology-based NSPS requirements for new sources; and

- NESHAPS requirements for new and existing sources of hazardous air pollutants.

Table 3.1 lists the entities affected by the three different types of regulatory schemes and the citations wherein the various emission limitations and test procedures are given.

The Clean Air Act Amendments of 1970 and 1977 provide basic authority for EPA's continuous emission monitoring requirements on affected facilities. Basic provisions provide:

- Broad authority for developing regulations and carrying out the provisions of the Act; and
- Require State Implementation Plans, approved by EPA, to include CEM requirements on monitoring industrial source emissions as part of their permit approval.

The Act is divided into three titles:

- Title I: Air Pollution Prevention and Control

    Part A - Air Quality and Emission limitations;
    Part B - Ozone Protection;
    Part C - Prevention of Significant Deterioration of Air Quality;
    Part D - Plan requirements for nonattainment areas

- Title II: Emission Standards For Moving Sources

    Part A - Motor Vehicle Emission And Fuel Standards;
    Part B - Aircraft Emission Standards;

- Title III: General

Each title is divided into individual sections. Title I of the Clean Air Act Amendments of 1977 contains four sections which address applicability of CEMs to monitor source emissions.

- Section 105 - Grants for support of air pollution planning and control programs.

Section 105 provides for federal grants to develop and operate State air pollution control programs. Such grants may be made "upon such terms and conditions as the Administrator may find necessary to carry out the purpose of this Section." [If the State did not implement CEMs as part of its regulatory strategy, then the administrator may make implementation of a CEM program a condition for receiving a grant.]

- Section 110 (a) (2)(F) - Implementation plans.

Section 110(a)(2)(F) authorizes SIP approval if a SIP provides "... (ii) requirements for installation of equipment by owners or operators of stationary sources to monitor emissions from such sources:"

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TABLE 3.1
REGULATIONS UNDER THE CLEAN AIR ACT

Type of emission standard	Affected sources	Source of emission limitations and prescribed test procedures
Criteria Pollutant Standards - Standard set for the pollutant; applies to all sources of such pollutant (based on size); standards for emissions and source testing vary among the states	All facilities which emit particulate matter, sulfur oxides, nitrogen oxides, hydrocarbons, carbon monoxide, and lead.	State Implementation Plans and local ordinance (whichever are more stringent).
New Source Performance Standards - Standard set for the specific process (based on size); applies to all new processes of that type; nationwide test standards apply; existing sources are amendable to NSPS if such sources are substantially modified or rebuilt.	New facilities; fossil-fuel fired steam generators, incinerators, portland cement plants, nitric acid plants, sulfuric acid plants, asphalt concrete plants, petroleum refineries, storage vessels for petroleum liquids, secondary lead smelters, secondary brass and bronze ingot production plants, iron and steel plants, sewage treatment plants, primary aluminum industry, primary copper, zinc, and lead smelters, phosphate fertilizer industry operations, coal preparation plants, kraft pulp mills etc. Existing facilities: 1) Any of the above which exist prior to an NSPS but are subsequently modified. 2) Any of the above which emit a pollutant limited by the NSPS other than particulate, SO_x, NO_x, HC, and CO. The particular limitation is set by the state and may be less stringent than that applicable to new facilities.	Title 40, Code of Federal Regulations, Part 60(40 CFR 60)
Hazardous Pollutant Standards - Standard set for specific pollutant; applies to all sources of such pollutant; emission and test standards are nationwide in scope; no variation among state and local jurisdictions.	Specified facilities which emit asbestos, beryllium, mercury, benzene.	Title 40, Code of Federal Regulations, Part 61 (40 CFR 61).

IMPLEMENTATION PLANS

Sec. 110. (a) (1): "Each State shall, after reasonable notice and public hearings, adopt and submit to the Administrator, within nine months after the promulgation of a national primary ambient air quality standard (or any revision thereof) under section 109 for any air pollutant, a plan which provides for implementation, maintenance, and enforcement of such primary standard in each air quality control region (or portion thereof) within such State. In addition, such State shall adopt and submit to the Administrator (either as a part of a plan submitted under the preceding sentence or separately) within nine months after the promulgation of a national ambient air quality secondary standard (or revision thereof), a plan which provides for implementation, maintenance, and enforcement of such secondary standard in each air quality control region (or portion thereof) within such State. Unless a separate public implementing such secondary standard at the hearing required by the first sentence of this paragraph."

"(2) The Administrator shall, within four months after the date required for submission of a plan under paragraph (1), approve or disapprove such plan for each portion thereof. The Administrator shall approve such plan, or any portion thereof, if he determines that it was adopted after reasonable notice and hearing and that --"

CEM REPORTING REQUIREMENTS

Section 110(a) (2) (F) also conditions SIP approval on inclusion of provisions for "(iii) for periodic reports on the nature and amounts of such emissions; (iv) that such reports shall be correlated by the State Agency with any emission limitations or standards established pursuant to this Act, which reports shall be available at reasonable times for public inspection..."

Section 110(a) (2) (F) also provides (i) necessary assurances that the State will have adequate personnel, funding, and authority to carry out such implementation plan, (ii) requirements for installation of equipment by owners or operators of stationary sources to monitor emissions from such sources, (iii) for periodic reports on the nature and amounts of such emissions; (iv) that such reports shall be correlated by the State agency with any emission limitations or standards established pursuant to this Act, which reports shall be available at reasonable times for public inspection; (v) for authority comparable to that in section 303, and adequate contingency plans to implement such authority; and (vi) requirements that the State comply with the requirements respecting State boards under section 128;"

- Section 113 - Federal Enforcement

Section 113(d) (1) (C) provides that delayed compliance orders (DCO) are to require "the emission monitoring and reporting authorized to be required under §§ 110 (a) (2) (F) and 114 (a) (1) ..."

Section 113(d)(1) also states: " *A State (or, after thirty days notice to the State, the Administrator) may issue to any stationary source which is unable to comply with any requirement of an applicable implementation plan an order which specifies a date for final compliance with such requirement later than the date for attainment of any national ambient air quality standard specified in such plan ...*"

"*(C) the order requires compliance with applicable interim requirements as provided in paragraph (5) (B) (relating to sources converting to coal), and paragraaphs (6) and (7) (relating to all sources receiving such orders) and requires the emission monitoring and reporting by the source authorized to be required under sections 110(a) (2) (F) and 114(a) (1):*"

o Section 114 - Inspections, Monitoring and Entry

Section 114 (a) (1) provides that the Administrator may require for the purpose of developing certain regulations, determining violations, or "carrying out any provision of this Act," a source to "...(C) install, use, and maintain such monitoring equipment or methods, (D) sample such emissions (in accordance with such methods, at such locations, at such intervals, and in such a manner as the Administrator shall prescribe), and (E) provide such other information, as he may reasonably require..."

INSPECTION, MONITORING, AND ENTRY

Further, Sec. 114. "(a) For the purpose (i) of developing or assisting in the development of any implementation plan under section 110 or 111(d), any standard of performance under section 111, or any emission standard under section 112 (ii) of determing whether any person is in violation of any such standard or any requirement of such a plan, or (iii) carrying out any provision of this Act (except a provision of title II with respect to a manufacturer of new motor vehicles or new motor vehicle engines) --"

(1) the Administrator may require any person who owns or operates any emission source or who is subject to any requirement of this Act (other than a manufacturer subject to the provisions of section 206 (c) or 208 with respect to a provision of Title II to (A) establish and maintain such records, (B) make such reports, (C) install, use, and maintain such monitoring equipment or methods, (D) sample such emissions (in accordance with such methods, at such locations, at such intervals, and in such manner as the Administrator shall prescribe), and (E) provide such other information, as he may reasonably require.

3.3 FEDERAL REGISTER AND CODE OF FEDERAL REGULATIONS

The Clean Air Act of 1970 was implemented by Congress to provide a well-planned manner by which pollutant sources could be regulated. Basically, two types of sources were addressed: stationary and mobile. Congress intended to control both new and existing sources. The Clean Air Act gave broad authority in implementing its provisions. In the preceding section, we have addressed the authority given to EPA in association with continuous emission monitoring requirements. The Act is the foundation for this authority. Regulations passed by Congress are recorded in two publications:

- o Federal Register, and
- o Code of Federal Regulations.

The Federal Register (FR) is published daily by the U.S. Congress. It provides information associated with the business of the Congress proposed and promulgated regulations, amendments to previously promulgated regulations, and other announcements associated with all government agencies.

Those entries into the Federal Register which address continuous emission monitoring and its application to industrial sources and Kraft pulp mills in particular are outlined in Table 3.2.

TABLE 3.2
FEDERAL REGISTER ENTRIES APPLICABLE TO CONTINUOUS EMISSION MONITORING

Dec. 23, 1971	36 FR 24877	The U.S. Environmental Protection Agency published regulations affecting selective facilities requiring performance testing, stack gas monitoring, record keeping and reporting requirements. Those affected facilities were fossil-fuel fired steam generators, Portland cement plants, nitric acid plants, sulfuric acid plants and incinerators. As part of this regulation, Reference Methods 1 through 8 were promulgated, as Appendix A.
March 8, 1974	39 FR 9320	Federal Reference Method 11 - Determination of Hydrogen Sulfide Emissions from Stationary Sources - was promulgated as a Reference Method. The method involves extracting a sample into a series of impingers containing cadmium hydroxide ($Cd(OH)_2$). Cadmium sulfide participates out and is titrated with iodine to an equivalent end point.
Oct. 6, 1975	40 FR 46240	Simultaneous rulemaking addressing enforceable procedures requiring new and existing sources to monitor emissions on a continuous basis. o Part 51 - Requirements for the preparation, adoption and submittal of implementation plans o Appendix P - Minimum emission requirements

TABLE 3.2 (contd.)
FEDERAL REGISTER ENTRIES APPLICABLE TO CONTINUOUS EMISSION MONITORING

		o Part 60 - Standards of Performance for New Stationary Sources ... o Appendix B - Performance Specification
Sept. 24, 1976	41 FR 42012	Proposed standards of performance for new, modified and reconstructed Kraft pulp mill.
May 23, 1977	42 FR 26205	Use of methods other than Reference Method 9 to be used as a means of measuring plume opacity.
Aug. 18, 1977	42 FR 41754	Published in the Federal Register were revisions relating to the Reference Methods. Those of interest are:
		RM 1: Sampling and Velocity Traverses for Stationary Sources;
		RM 2: Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)
		RM 3: Gas analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight;
		RM 4: Determination of Moisture Content in Stack Gases
		RM 6: Determination of Sulfur Dioxide Emissions from Stationary Sources.
Jan. 10, 1978	43 FR 1495	On Jan. 10, 1978, revision to Federal Reference Method 11 were incorporated into the Federal Register. EPA found that interferences resulting from the presence of mercaptans in some refinery fuel gases could lead to erroneous test data. The revision involved a new absorbing solution was incorporated into the Reference Method.
Feb. 23, 1978	43 FR 7568	Standards of Performance for new modified and reconstructed Kraft pulp mills.

TABLE 3.2 (contd.)
FEDERAL REGISTER ENTRIES APPLICABLE TO CONTINUOUS EMISSION MONITORING

		Federal Reference Methods added o Method 16 - Semicontinuous determination of sulfur emissions from stationary sources o Method 17 - Determination of particulate emissions from stationary sources (In-stack filtration method)
Aug. 7, 1978	43 FR 34784	This action amends the standard of performance for Kraft pulp mills by adding a provision of determining compliance of attended facilities which use a control system incorporating a process other than combustion. o O_2 correction to untreated emission points of total reduce sulfur in cases of brown stock washers, black liquor oxidation systems or digestor systems.
Jan. 12, 1979	44 FR 1578	This action amends FRM 16 for determining total reduced sulfur emissions from stationary sources. The admendment corrects several typographical errors and improves the Reference Method by requiring the use of a scrubber to prevent possible interference from high concentrations of SO_2.
Aug.8, 1979	44 FR 46481	Advance notice of proposed rulemaking (ANPR) directing revisions of Part 51 involving state requirements on affected facilities to monitor emissions on a continual basis.
Oct. 10, 1979	44 FR 58602	Proposed revisions to Performance Specification Test 1, 2 and 3.

TABLE 3.2 (contd.)
FEDERAL REGISTER ENTRIES APPLICABLE TO CONTINUOUS EMISSION MONITORING

June 18, 1981	46 FR 31904	Proposed test method for determining total reduced sulfur (TRS) from Kraft pulp mills. o Method 16A: Determination of total reduced sulfur emissions from stationary source (Impinger Technique).
July 20, 1981	46 FR 37287	Proposed Performance Specification 5 (PS5) for continuous emission monitoring of total reduced sulfur (TRS) emissions from Kraft pulp mills.
March 30, 1983	48 FR 13322	Promulgation of revisions to Performance Specification Test 1, specification and test procedures for opacity continuous emission monitoring systems in stationary sources.
May 25, 1983	48 FR 23608	Promulgation of revisions to the performance specifications for continuous emission monitoring systems (CEM's) for sources subject to Performance Specification 2 and 3.
July 20, 1983	48 FR 32984	Promulgation of Performance Specification 5 - Specifications and Test Procedures for TRS Continuous Emission Monitoring Systems in Stationary Sources.
Sept. 30, 1983	48 FR 45034	On September 30, 1983, revision to Federal Reference Method 1 were published in the Federal Register. The revisions addressed reduction in number of sampling points required for sampling and velocity traverses from stationary sources without affecting accuracy.
March 14, 1984	49 FR 9676	Proposed Appendix F, Procedure 1 adding quality assurance requirements to gas continuous emission monitoring systems (CEMs) when the CEMs are used as the method for showing compliance with emission limits on a continuous basis.
Aug. 17, 1984	49 FR 32987	The purpose of this action is to propose amendments to 60.284 of Subpart BB of 40 CFR Part 60 to allow the monitoring and use of CO_2 to correct the measured total reduced sulfur (TRS) concentration emitted from Kraft pulp mill recovery furnaces.

TABLE 3.2 (contd.)
FEDERAL REGISTER ENTRIES APPLICABLE TO CONTINUOUS EMISSION MONITORING

Feb. 14, 1985	50 FR 6316	Amendment and innovative technology waiver for New Source Performance Standards for Kraft pulp mills.
March 8, 1985	50 FR 9578	Promulgated Federal Reference Method 16A as an alternative to Federal Reference Method 16.

3.4 FEDERAL REGISTER, OCTOBER 6, 1975

On October 6, 1975, the U. S. Environmental Protection Agency (EPA) adopted requirements for the continuous emission monitoring of certain new and existing sources. The requirements for existing sources were adopted under 40 CFR Part 51, Requirements for the Preparation, Adoption and Submittal of Implementation Plans. The requirements for new sources were adopted under 40 CFR Part 60, Standards of Performance for New Stationary Sources. These regulations appeared in the Federal Register as 40 FR 46256, October 6, 1975. The continuous monitoring requirements adopted by EPA are minimum requirements. State and local agencies may, at their discretion, adopt more comprehensive or stringent requirements.

Figure 3.1 illustrates the connection between existing sources and new sources as outlined in 40 FR 46256, October 6, 1975.

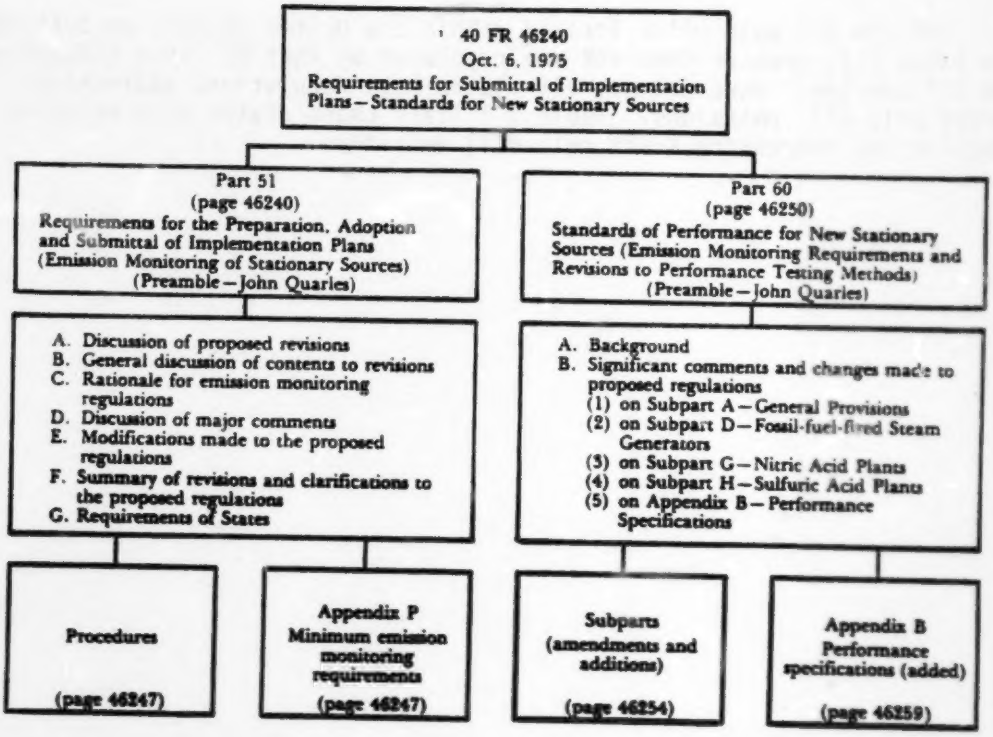
40 FR 46240
Oct. 6. 1975
Requirements for Submittal of Implementation Plans—Standards for New Stationary Sources
Part 51
(page 46240)
Requirements for the Preparation, Adoption and Submittal of Implementation Plans (Emission Monitoring of Stationary Sources)
(Preamble—John Quarles)
Part 60
(page 46250)
Standards of Performance for New Stationary Sources (Emission Monitoring Requirements and Revisions to Performance Testing Methods)
(Preamble—John Quarles)
A. Discussion of proposed revisions
B. General discussion of contents to revisions
C. Rationale for emission monitoring regulations
D. Discussion of major comments
E. Modifications made to the proposed regulations
F. Summary of revisions and clarifications to the proposed regulations
G. Requirements of States
A. Background
B. Significant comments and changes made to proposed regulations
(1) on Subpart A—General Provisions
(2) on Subpart D—Fossil-fuel-fired Steam Generators
(3) on Subpart G—Nitric Acid Plants
(4) on Subpart H—Sulfuric Acid Plants
(5) on Appendix B—Performance Specifications
Procedures
(page 46247)
Appendix P
Minimum emission monitoring requirements
(page 46247)
Subparts
(amendments and additions)
(page 46254)
Appendix B
Performance specifications (added)
(page 46259)

Figure 3.1. Federal Register, October 6, 1975

The date of construction and the date of promulgation of a regulation will determine whether a Kraft pulp mill is classified as a "new" source or an "existing" source. Once again, "new" sources are regulated under 40 CFR Part 60, while "existing" sources are regulated under 40 CFR Part 51. These sources covered under 40 CFR Part 60 and termed NSPS sources, while those covered under 40 CFR Part 51 are termed SIP sources.

The SIP regulations require that specific categories of industrial sources shall install continuous monitoring systems to monitor emissions of sulfur dioxide, oxides of nitrogen and opacity. In certain cases, it is also required to monitor carbon dioxide or oxygen so that the output from the SO_2 and NO_x monitors can be converted to units of the standard. The regulations include requirements for design and performance specifications, procedures for conducting performance evaluations, and requirements for record keeping.

Even though the original regulations for SIP sources did not address Kraft pulp mills, many states, as part of their own SIP program, require continuous TRS emission monitoring. Regulations under 40 CFR 51 are minimum monitoring requirements. The state requirements can be more strict than Part 51.

Of the 175 pulp mills located within the United States, as outlined in Table 2.2, greater than 90% are regulated by Part 51, thus classified as SIP sources. However, not all states have regulations addressing Kraft pulp mill emissions. Table 3.3 lists those states with existing regulations addressing Kraft pulp mill emissions.

TABLE 3.3
EXISTING STATE REGULATIONS ADDRESSING PULP MILLS

State	Total Reduced Sulfur (TRS) Emissions				
	General Pulp Mill	Lime Kiln	Recovery Furnace	Smelt Tank	Digester and Stripper
Alabama			1.2 lbs (as hydrogen sulfide) on a dry basis/ton air dry pulp (Daily avg/quarter)		
Alaska	20 lbs/TADP per 24 hours of SO_2 emissions				
Arizona		40 ppm as H_2S on a dry basis corrected to 10% O_2 as a 24-hr avg.	20 ppm as H_2S on a dry basis corrected to 8% O_2		
California					
Colorado		8 ppm as TRS on a dry basis corrected to 10% O_2 as a 24-hr avg.	Straight - 5 ppm by volume on a dry basis, corrected to 8% O_2 Cross - 25 ppm by volume on a dry basis, corrected to 8% O_2	0.0084 g/kg Black liquor solids	5 ppm by volume on a dry basis, corrected to 10% O_2
Florida			New Plant - 1 ppm as H_2S on a dry basis Existing Plant - 17.5 ppm as H_2S on a dry basis		
Georgia		40 ppm as TRS on a dry basis corrected to 10% O_2 as a 24-hr avg.	Old - 20 ppm of TRS on a dry basis corrected to 8% O_2 (before Sept. 24, 1976) on 24-hr avg. New - 5 ppm of TRS on a dry basis corrected to 8% O_2 (After Sept. 24, 1976) on 24-hr avg. Cross - 25 ppm of TRS on a dry basis corrected to 8% O_2	0.0168 lbs/ton Black liquor solids	5 ppm by volume on a dry basis, corrected to 10% O_2
Hawaii					

TABLE 3.3 (Continued)
EXISTING STATE REGULATIONS
ADDRESSING PULP MILLS

	Total Reduced Sulfur (TRS) Emissions				
State	General Pulp Mill	Lime Kiln	Recovery Furnace	Smelt Tank	Digester and Stripper
Idaho		40 ppm or 0.2 lbs of sulfur/ton ADP	General Provisions 0.5 lbs of sulfur/ton ADP or 17.5 ppm as H_2S on dry basis for average daily emission. 2.0 lbs of sulfur/ton ADP or 70 ppm as H_2S on Dry basis for average daily emission New Sources 5 ppm as a daily arithmetic average or 0.12 lbs of sulfur/ton ADP on a daily average 40 ppm for any sixty (60) consecutive minutes		
Kentucky		8 ppm corrected to 10% O_2	Existing 15 ppm as an arithmetic average over any consecutive 24-hr period 40 ppm for more than 60 total minutes in any 24-hr period New Straight 5 ppm corrected to 8% O_2 Cross 25 ppm corrected to 8% O_2	0.0084 g/kg Black liquor solids	5 ppm corrected to 8% O_2
Louisiana		20 ppm corrected to 8% O_2	New Straight-New design 5 ppm corrected to 8% O_2 Straight-Old design 20 ppm corrected to 8% O_2 Cross Recovery 25 ppm corrected to 8% O_2	0.0084 g/kg Black liquor solids	5 ppm corrected to 10% O_2

TABLE 3.3 (Continued)
EXISTING STATE REGULATIONS
ADDRESSING PULP MILLS

State	Total Reduced Sulfur (TRS) Emissions				
	General Pulp Mill	Lime Kiln	Recovery Furnace	Smelt Tank	Digester and Stripper
Maryland	0.6 lbs/ton of oven-dired unbleached Kraft pulp			0.087 lb/1000 lb Black liquor solids	
Montana			0.087 pounds/1000 pounds of black liquor or 1.75 ppm as H_2S on a dry basis		
New Hampshire			2 lbs/ton ADP		
New Mexico	0.2 lbs/ton ADP		0.1 lbs of sulfur as H_2S/tons ADP		
New York		20 ppm	Old Design - 20 ppm New Design - 5 ppm Cross - 25 ppm	0.0168 lbs/ton black liquor solids	5 ppm corrected to 10% O_2
North Carolina		20 ppm	Old Design - 20 ppm New Design - 5 ppm Cross - 25 ppm	0.0168 lbs/ton black liquor solids	5 ppm corrected to 10% O_2
Oregon		8.0 ppm corrected to 10% O_2	Straight - 5 ppm corrected to 8% O_2 Cross - 25 ppm corrected to 8% O_2	0.0168 lbs/ton black liquor solids	5.0 ppm by volume on a dry basis, corrected to actual O_2 content of untreated gas stream
South Carolina		20.0 ppm corrected to 10% O_2	Cross - 25 ppm avg. corrected to 8% O_2 over 12 hr Old Design - 20 ppm average corrected to 8% O_2 over 12 hr New Design - 5 ppm average corrected to 8% O_2 over 12 hr	0.0084 g/kg Black liquor solids	5.0 ppm

TABLE 3.3 (Continued)
EXISTING STATE REGULATIONS
ADDRESSING PULP MILLS

State	Total Reduced Sulfur (TRS) Emissions				
	General Pulp Mill	Lime Kiln	Recovery Furnace	Smelt Tank	Digester and Stripper
Tennessee		40.0 ppm corrected to 10% O_2	20 ppm by volume, expressed as H_2S on a dry basis, corrected to 8% O_2 on a 24-hr avg. basis	0.0084 g/kg black liquor solids	5.0 ppm by volume on a dry basis, corrected to 10% O_2
Virginia	1.2 lbs of total reduced sulfur as H_2S/ton air dryed pulp (daily average/quarter)				
Washington		8 ppm as H_2S for more than 2 consecutive hours/day 50 ppm as TRS for avg. daily emission 20 ppm as TRS for avg. daily emission corrected to 10% O_2 after Jan. 1, 1985	Old - 17.5 corrected to 8% O_2 on a daily average (before Jan. 1, 1970) New - 5.0 ppm corrected to 8% O_2 on a daily avg. (after Jan. 1 1970)		
Wisconsin		8 ppm as TRS by volume on a dry basis, corrected to 10% O_2	Straight - 5 ppm by volume on a dry basis, corrected to 8% O_2 Cross - 25 ppm by volume on a dry basis, corrected to 8% O_2	0.0084 g/kg black liquor solids	5 ppm by volume on a dry basis, corrected to 10% O_2

Table 3.3 demonstrates the wide variation in regulations imposed on pulp mills regulated under Part 51 of the regulations. Some mills are subject to emission limits of total reduced sulfur (TRS), while others are limited as to sulfur dioxide (SO_2) emissions. Still others are limited by ambient air standards around the regulated facility.

Presently, there are twenty-six (26) Kraft pulp mills within the United States that fall under New Source Performance Standards. This represents approximately 20% of the Kraft pulp mill population. Table 3.4 lists those mills currently affected by the NSPS regulations.

TABLE 3.4
KRAFT PULP MILLS
AFFECTED BY NSPS REGULATIONS

Company	Location	Sources Covered Under NSPS
Stone Container	Port Wentworth, Georgia	Recovery Furnace Smelt Dissolving Tank Lime Kiln
Buckeye Cellulose	Oglethorpe, Georgia	Recovery Furnace Smelt Dissolving Tank Lime Calciner Digerster Multiple-Effect Evaporators Brown Stock Washer System Condensate Stripping System
Western Kraft	Hawesville, Ky.	Lime Kiln Brown Stock Washer System
Stone Container	Hodge, Louisiana	Multiple-Effect Evaporators
International Paper	Mansfield, Louisiana	Recovery Furnace Smelt Dissolving Tank Lime Kiln Digesters Multiple-Effect Evaporators Brown Stock Washer System
Boise Cascade	Rumford, Maine	Recovery Furnace Smelt Dissolving Tank
Champion International	Missoula, Montana	Recovery Furnace Smelt Dissolving Tank Lime Kiln Digester Multiple-Effect Evaporators

TABLE 3.4 (Continued)
KRAFT PULP MILLS
AFFECTED BY NSPS REGULATIONS

Company	Location	Sources Covered Under NSPS
Federal Paperboard	Riegelwood, North Carolina	Digesters Multiple-Effect Evaporators
Boise Cascade	St. Helens, Oregon	Lime Kiln
International Paper	Gardiner, Oregon	Recovery Furnace Smelt Dissolving Tank Lime Kiln Digester Multiple-Effect Evaporators Condensate Stripper System Brown Stock Washer Systems
International Paper	Georgetown, S.C.	Lime Kiln
Tennessee River	Counce, Tennessee	Recovery Furnace Smelt Dissolving Tank
Champion International	Courtland, Alabama	Recovery Furnace Smelt Dissolving Tank Lime Kiln Digester Black Liquor Oxidation System Multiple-Effect Evaporators Brown Stock Washer System Digesters (2)
Container Corporation	Brewton, Alabama	Digesters
Hammermill Paper	Selma, Alabama	Recovery Furnace Smelt Dissolving Tank Lime Kiln Multiple-Effect Evaporators Digesters Brown Stock Washer System
Nekoosa Paper	Ashdown, Arkansas	Recovery Furnace Smelt Dissolving Tank Lime Kiln Black Liquor Oxidation System Digesters Multiple-Effect Evaporators Brown Stock Washer System

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TABLE 3.4 (Continued)
KRAFT PULP MILLS
AFFECTED BY NSPS REGULATIONS

Company	Location	Sources Covered Under NSPS
Georgia-Pacific	Crossett, ARkansas	Recovery Furnace Smelt Dissolving Tank Lime Kiln Multiple-Effect Evaporators
Simpson Paper	Anderson, California	Lime Kiln
Buckeye Cellulose	Perry, Florida	Lime Calciner
Container Corporation	Fernandina Beach,	Cross Recovery Furnace Smelt Dissolving Tank
Georgia Kraft	Rome, Georgia	Lime Kiln
Stone Container	Hopewell, Virginia	Recovery Furnace Smelt Dissolving Tank
Crown Zellerbach	Camas, Washington	Lime Kiln

Sources covered under NSPS Regulations, like the SIP regulations, have specific monitoring and reporting requirements associated with particulate and total reduced sulfur emissions. A thorough understanding of both of these regulations is important in any environmental agency.

3.4.1 Existing Source Regulations (40 CFR 51)

The requirements for existing sources to install continuous monitoring systems were designed to partially implement the requirements of Sections 110 (a) (2) (F) (ii) and (iii) of the Clean Air Act, which state that implementation plans must provide "requirements for installation of equipment by owners or operators of stationary sources to monitor emissions from such sources", and "for periodic reports on the nature and amounts of such emissions". However, the original implementation plan requirements did not require SIP's to contain legally enforceable procedures mandating continuous emission monitoring and recording. At the time the original requirements were published, EPA had accumulated little data on the availability and reliability of continuous monitoring devices. The Agency believed that the state-of-the-art was such that it was not prudent to require existing sources to install such devices.

Since that time, much work has been done by EPA and others to field test and compare various continuous emission monitors. As a result of this work, the Agency now believes that for certain sources, performance specifications for accuracy, reliability and durability can be established for continuous emission monitors of oxygen, carbon dioxide, sulfur dioxide, and oxides of nitrogen and for the continuous measurement of opacity. Accordingly EPA adopted the requirements now contained at 40 CFR 51.19(e) which requires states to revise their implementation plans to include legally enforceable procedures to require certain stationary sources to install, calibrate, maintain, and operate equipment for continuously monitoring and recording emissions. The specific stationary sources and pollutants to be monitored are identified in 40 CFR 51, Appendix P - Minimum Emission Monitoring Requirements. The specific source categories covered by the requirements are:

1. Fossil Fuel Fired Steam Generators
2. Fluid Bed Catalytic Cracking Unit Catalyst Regenerators
3. Sulfuric Acid Plants
4. Nitric Acid Plants
5. Portland Cement Plants

Appendix P outlines the specifics of the applicability of the continuous monitoring regulations regarding size (throughput) limitations for the affected facilities, the pollutants that must be monitored, exemptions, performance specifications and evaluation procedures , data reduction and maintenance requirements, and special considerations regarding alternative procedures. As indicated in Table 3.5, many states have expanded the initial five (5) source categories to include Kraft pulp mills. Consequently, the following specific regulation will apply to most existing Kraft pulp mills.

Section 51.19(e) requires that SIPs include "(1) equally enforceable procedures to require stationary sources subject to emissions standards.. to install, calibrate, maintain and operate equipment for continuously monitoring and recording emissions...".

Section 51.19(e) (3) and (4) require that SIPs also require maintenance of files on "emissions measurements...performance testing measurements, performance evaluations, calibration checks, and adjustments and maintenance..." and that the information be submitted to EPA as required in Appendix P.

§ 51.19 Source surveillance.

Each plan shall provide for monitoring the status of compliance with any rules and regulations which set forth any portion of the control strategy. Specifically, each plan shall, as a minimum, provide for:

(e) Legally enforceable procedures to require stationary sources subject to emission standards as part of an applicable plan to install, calibrate, maintain, and operate equipment for continuously monitoring and recording emissions; and to provide other information as specified in Appendix P of this part.

Installation

(1) Such procedures shall identify the types of sources, by source category and capacity, that must install such instruments, and shall identify for each source category the pollutants which must be monitored.

(2) Such procedures shall, as a minimum, require the types of sources set forth in Appendix P of this part (as such appendix may be amended from time to time) to meet the applicable requirements set forth therein.

(3) Such procedures shall contain provisions which require the owner or operator of each source subject to continuous emission monitoring and recording requirements to maintain a file of all pertinent information. Such information shall include emission measurements, continuous monitoring system performance testing measurements, performance evaluations, calibration checks, and adjustments and maintenance performed on such monitoring systems and other reports and records required by Appendix P of this Part for at least two years following the date of such measurements or maintenance.

Record-keeping

(4) Such procedures shall require the source owner or operator to submit information relating to emissions and operation of the emission monitors to the State to the extent described in Appendix P as frequently or more frequently as described therein.

Reporting

(5) Such procedures shall provide that sources subject to the requirements of § 51.19(e)(2) of this section shall have installed all necessary equipment and shall have begun monitoring and recording within 18 months of (1) the approval of a State plan requiring monitoring for that source or (2) promulgation by the Agency of monitoring requirements for that source. However, sources that have made good faith efforts to purchase, install, and begin the monitoring and recording of emission data but who have been unable to complete such installation within the time period provided may be given reasonable extensions of time as deemed appropriate by the State.

(6) States shall submit revisions to the applicable plan which implement the provisions of this section by October 6, 1976.

[40 FR 46240, October 6, 1975]

Appendix P of 40 CFR Part 51 sets forth the minimum requirements for continuous emission monitoring and reporting that each State Implementation Plans must include. At a minimum, these requirements include:

- Source categories to be affected - emission monitoring, recording and reporting requirements;
- Performance Specifications - addressing accuracy, reliability and durability of acceptable continuous emission monitoring systems;
- Units of the Standard - Techniques to convert emission data to units of the applicable State Emission Standard.

Section 1.0 of Appendix P of 40 CFR 51 states that CEM data may be used for: "Such data may be used directly or undirectly for compliance determination or any other purpose deemed appropriate by the State. Though the monitoring requirements are specified in detail, States are given some flexibility to resolve difficulties that may arise during the implementation of these regulations".

More importantly, Section 3.1 of Appendix P of 40 CFR 51 referenced the performance specifications test which must be used to determine acceptability of the installed continuous emission monitoring equipment as required on affected facilities outlined in Section 1.1.1.

3.1 *Performance specifications.*

The performance specifications set forth in Appendix B of Part 60 are incorporated herein by reference, and shall be used by States to determine acceptability of monitoring equipment installed pursuant to this Appendix except that (1) where reference is made to the "Administrator" in Appendix B, Part 60, the term "State" should be inserted for the purpose of this Appendix (e.g., in Performance Specification 1, 1.2, "... monitoring systems subject to approval by the *Administrator,*" should be interpreted as, "... monitoring systems subject to approval by the *State*"), and (2) where reference is made to the "Reference Method" in Appendix B, Part 60, the State may allow the use of either the State approved reference method or the Federally approved reference method as published in Part 60 of this Chapter. The Performance Specifications to be used with each type of monitoring system are listed below.

Performance Specifications

3.1.1 Continuous monitoring systems for measuring opacity shall comply with Performance Specification 1.

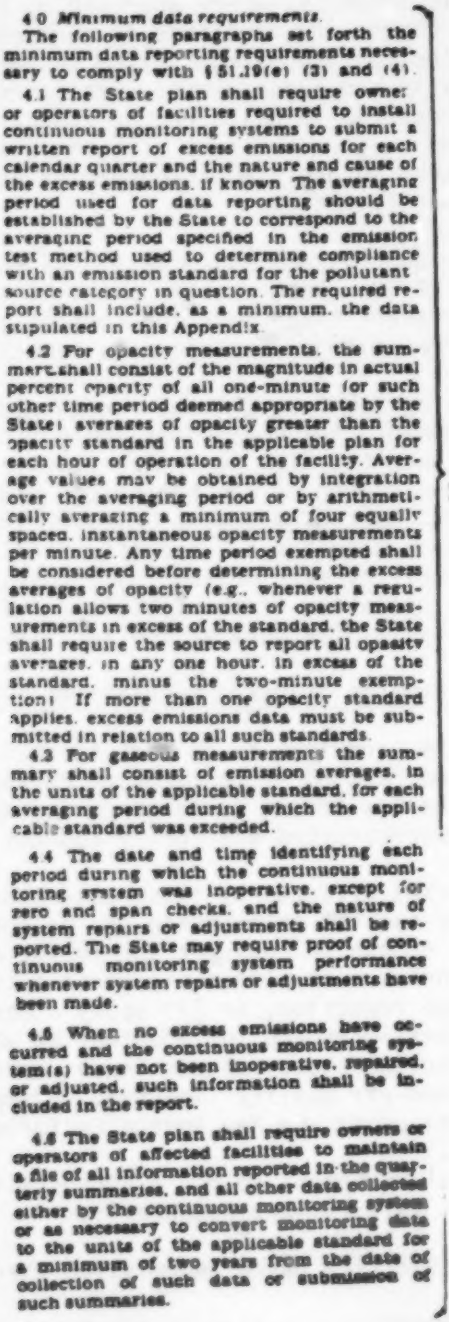
3.1.2 Continuous monitoring systems for measuring nitrogen oxides shall comply with Performance Specification 2.

3.1.3 Continuous monitoring systems for measuring sulfur dioxide shall comply with Performance Specification 2.

3.1.4 Continuous monitoring systems for measuring oxygen shall comply with Performance Specification 3.

3.1.5 Continuous monitoring systems for measuring carbon dioxide shall comply with Performance Specification 3.

Finally, within Section 4.0 of Appendix P of 40 CFR 51, minimum data requirements are established. Addressed in this section are data acquisiton and storage requirements, reporting requirements of excess emissions and data reduction procedures.



4.0 *Minimum data requirements.*

The following paragraphs set forth the minimum data reporting requirements necessary to comply with § 51.19(e) (3) and (4).

4.1 The State plan shall require owners or operators of facilities required to install continuous monitoring systems to submit a written report of excess emissions for each calendar quarter and the nature and cause of the excess emissions, if known. The averaging period used for data reporting should be established by the State to correspond to the averaging period specified in the emission test method used to determine compliance with an emission standard for the pollutant source category in question. The required report shall include, as a minimum, the data stipulated in this Appendix.

4.2 For opacity measurements, the summary shall consist of the magnitude in actual percent opacity of all one-minute (or such other time period deemed appropriate by the State) averages of opacity greater than the opacity standard in the applicable plan for each hour of operation of the facility. Average values may be obtained by integration over the averaging period or by arithmetically averaging a minimum of four equally spaced, instantaneous opacity measurements per minute. Any time period exempted shall be considered before determining the excess averages of opacity (e.g., whenever a regulation allows two minutes of opacity measurements in excess of the standard, the State shall require the source to report all opacity averages, in any one hour, in excess of the standard, minus the two-minute exemption). If more than one opacity standard applies, excess emissions data must be submitted in relation to all such standards.

4.3 For gaseous measurements the summary shall consist of emission averages, in the units of the applicable standard, for each averaging period during which the applicable standard was exceeded.

4.4 The date and time identifying each period during which the continuous monitoring system was inoperative, except for zero and span checks, and the nature of system repairs or adjustments shall be reported. The State may require proof of continuous monitoring system performance whenever system repairs or adjustments have been made.

4.5 When no excess emissions have occurred and the continuous monitoring system(s) have not been inoperative, repaired, or adjusted, such information shall be included in the report.

4.6 The State plan shall require owners or operators of affected facilities to maintain a file of all information reported in the quarterly summaries, and all other data collected either by the continuous monitoring system or as necessary to convert monitoring data to the units of the applicable standard for a minimum of two years from the date of collection of such data or submission of such summaries.

Reporting Requirements

The SIP should provide for quarterly reporting by source operators of excess emissions. The reports must contain data regarding excess emissions and periods when the continuous monitoring equipment was inoperative (40 CFR 51, Appendix P, Paragraph 4). If neither situation occured during the quarter, a report documenting the absence of these events must still be filed.

The reports should identify, where applicable, the cause of excess emissions, the dates, times, and magnitude of such emissions and the dates and times when the continuous monitoring system was inoperative and the nature of repairs and adjustments. Excess emissions for gaseous pollutants should be reported in units of the standard; the averaging time should be required to be consistent with the averaging period specified in the emission test method used to determine compliance with the applicable SIP emission limitation.

Data reduction procedures are essentially the same as required for new sources under 40 CFR 60. However, the units of the SIP emission limitations may be different than those for sources subject to NSPS, thus requiring some alteration of certain data reduction procedures.

In Appendix P, Paragraph 6.0, EPA has recognized the difficulty in setting uniform requirements for continuous monitoring systems at existing facilities and has allowed the SIPs to include flexible requirements that will not impede the development of new technology and will provide the minimum installation and operating costs. Alternative monitoring requirements may be adopted on a case basis. Specific problems that may be encountered at a given facility may include (1) condensed water vapor in the stack, (ii) infrequent operation of the facility, (iii) extreme economic burden, and (iv) physical limitations at the facility.

3.4.2 New Source Performance Standard Regulations (40 CFR 60)

Concurrent with the promulgation of Part 51 dealing with existing sources, EPA promulgated Part 60 - Standards of Performance for New Stationary Sources. The New Source Performance Standards (NSPS) apply to new, modified and reconstructed stationary sources of air pollution.

The source categories affected by these standards are those which have been identified by the EPA as emitting one or more pollutants in quantities significant enough to endanger the public health or welfare. Under NSPS these categories must either (1) achieve the degree of emission limitation or percentage reduction, or (2) apply a design, equipment, work practice, operational standard, or combination which reflects the best available technological system of continuous emission reduction (considering cost and non-air quality impacts). Examples of control methods currently in use under the New Source Performance Standards are:

- Control equipment (e.g., electrostatic precipitators, fabric filters, wet scrubbers),
- Fuel selection based on emission characteristics,
- Precombustion cleaning or treatment of fuels,

- Use of a production process which is inherently low polluting or nonpolluting, and
- Use of particular work practices and/or operational standards so as to decrease emissions.

Within Subpart A of 40 CFR 60, General Provisions, are outlined basic emission monitoring requirements such as: (1) notification and recordkeeping requirements; (2) requirement that the monitoring systems not only meet, but are demonstrated or certified to meet, certain design and performance specifications; and (3) requirements for proper location of the monitor in ducts or stacks. Data reduction and calculation procedures are also specified. All sources affected by NSPS have to comply with these general provisions of the regulations.

Requirements for new sources associated with CEM recordkeeping and reporting requirements are covered under Section 60.7.

REQUIREMENTS FOR NEW SOURCES
40 C.F.R. Part 60, Subpart A (General Provisions)
CEM RECORDKEEPING AND REPORTING REQUIREMENTS (Section 60.7)

(b) Any owner or operator subject to the provisions of this part shall maintain records of the occurrence and duration of any startup, shutdown, or malfunction in the operation of an affected facility; any malfunction of the air pollution control equipment; or any periods during which a continuous monitoring system or monitoring device is inoperative.

Record-keeping

(c) Each owner or operator required to install a continuous monitoring system shall submit a written report of excess emissions (as defined in applicable subparts) to the Administrator for every calendar quarter. All quarterly reports shall be postmarked by the 30th day following the end of each calendar quarter and shall include the following information:

(1) The magnitude of excess emissions computed in accordance with § 60.13(h), any conversion factor(s) used, and the date and time of commencement and completion of each time period of excess emissions.

(2) Specific identification of each period of excess emissions that occurs during startups, shutdowns, and malfunctions of the affected facility. The nature and cause of any malfunction (if known), the corrective action taken or preventative measures adopted.

(3) The date and time identifying each period during which the continuous monitoring system was inoperative except for zero and span checks and the nature of the system repairs or adjustments.

(4) When no excess emissions have occurred or the continuous monitoring system(s) have not been inoperative, repaired, or adjusted, such information shall be stated in the report.

Reporting

(d) Any owner or operator subject to the provisions of this part shall maintain a file of all measurements, including continuous monitoring system, monitoring device, and performance testing measurements; all continuous monitoring system performance evaluations; all continuous monitoring system or monitoring device calibration checks; adjustments and maintenance performed on these systems or devices; and all other information required by this part recorded in a permanent form suitable for inspection. The file shall be retained for at least two years following the date of such measurements, maintenance, reports, and records.

Recordkeeping

Section 60.8 addresses performance test requirements of installed monitors.

§ 60.8 Performance tests.

(a) Within 60 days after achieving the maximum production rate at which the affected facility will be operated, but not later than 180 days after initial startup of such facility and at such other times as may be required by the Administrator under section 114 of the Act, the owner or operator of such facility shall conduct performance test(s) and furnish the Administrator a written report of the results of such performance test(s).

(b) Performance tests shall be conducted and data reduced in accordance with the test methods and procedures contained in each applicable subpart unless the Administrator (1) specifies or approves, in specific cases, the use of a reference method with minor changes in methodology, (2) approves the use of an equivalent method, (3) approves the use of an alternative method the results of which he has determined to be adequate for indicating whether a specific source is in compliance, or (4) waives the requirement for performance tests because the owner or operator of a source has demonstrated by other means to the Administrator's satisfaction that the affected facility is in compliance with the standard. Nothing in this paragraph shall be construed to abrogate the Administrator's authority to require testing under section 114 of the Act.

Tests in accordance with applicable subparts

§ 60.11 Compliance with standards and maintenance requirements.

(a) Compliance with standards in this part, other than opacity standards, shall be determined only by performance tests established by § 60.8, unless otherwise specified in the applicable standard.

Compliance Tests

(b) Compliance with opacity standards in this part shall be determined by conducting observations in accordance with Reference Method 9 in Appendix A of this part or any alternative method that is approved by the Administrator. Opacity readings of portions of plumes which contain condensed, uncombined water vapor shall not be used for purposes of determining compliance with opacity standards. The results of continuous monitoring by transmissometer which indicate that the opacity at the time visual observations were made was not in excess of the standard are probative but not conclusive evidence of the actual opacity of an emission, provided that the source shall meet the burden of proving that the instrument used meets (at the time of the alleged violation) Performance Specification 1 in Appendix B of this part, has been properly maintained and (at the time of the alleged violation) calibrated, and that the resulting data have not been tampered with in any way.

Use of Opacity CEM

(c) The opacity standards set forth in this part shall apply at all times except during periods of startup, shutdown, malfunction, and as otherwise provided in the applicable standard.

(d) At all times, including periods of startup, shutdown, and malfunction, owners and operators shall, to the extent practicable, maintain and operate any affected facility including associated air pollution control equipment in a manner consistent with good air pollution control practice for minimizing emissions. Determination of whether acceptable operating and maintenance procedures are being used will be based on information available to the Administrator which may include, but is not limited to, monitoring results, opacity observations, review of operating and maintenance procedures, and inspection of the source.

Start-up, Shut-down, Malfunctions

Not all NSPS source categories listed in Table 3.4 are required to apply continuous emission monitors as part of their performance standards. Performance standards for new souces are found in the Subparts of the Code of Federal Regulations. Monitoring requirements for each affected facility are found in these Subparts. Monitoring requirements for regulated pollutants are not enforceable until performance specifications have been promulgated for that pollutant. Table 3.5 list current continuous emission monitoring requirements for affected facilities. Those regulated pollutants where performance specification test have not been promulgated, thus that source not required to monitor, is indicated by an asterisk.

TABLE 3.5
NSPS SOURCES REQUIRING CONTINUOUS EMISSION MONITORING

Subpart	Facility	Continuous Emission Monitoring Requirements
Subpart D	FFFSG (construction commenced after August 17, 1971)	Opacity, SO_2 ,NO_x, O_2 or CO_2
Subpart Da	Fossil fuel fired electric utilities (construction commenced after September 18, 1978)	Opacity, SO_2, NO_x, O_2 or CO_2
Subpart G	Nitric Acid Plants (construction commenced after August 17, 1971)	NO_x
Subpart H	Sulfuric Acid Plants (construction commenced after August 17, 1971)	SO_2
Subpart J	Petroleum Refineries, (FCCU: construction commenced after June 11, 1983; Claus sulfur recovery unit: construction commenced after October 4, 1976)	Opacity, CO*, SO_2, H_2S*
Subpart P	Primary Copper Smelters (commenced construction after October 16, 1974)	Opacity, SO_2
Subpart Q	Primary Zinc Smelters (commenced construction after October 16, 1974)	Opacity, SO_2
Subpart R	Primary Zinc Smelters (commenced construction after October 16, 1974)	Opacity, SO_2
Subpart Z	Ferroalloy Production Facilities (commenced construction after October 21, 1974)	Opacity

Continued...

TABLE 3.5 (Continued)
NSPS SOURCES REQUIRING CONTINUOUS EMISSION MONITORING

Subpart	Facility	Continuous Emission Monitoring Requirements
Subpart AA	Electric Arc Furnaces (commenced construction after October 21, 1974)	Opacity
Subpart BB	Kraft Pulp Mills (commenced construction after September 24, 1976)	Opacity, TRS
Subpart HH	Lime Manufacturing Plants (commenced construction after May 3, 1977)	Opacity
Subpart NN	Phosphate Rock Plants (commenced construction after September 21, 1979)	Opacity
Subpart FFF	Flexible Vinyl and Urethane Coating and Printing (commenced construction after January 18, 1983)	VOC*

3.5 STANDARDS OF PERFORMANCE FOR KRAFT PULP MILLS - SUBPART BB

Subpart BB, Standards of Performance for Kraft Pulp Mills, addresses standards of performance, monitoring of emissions, test methods and procedures. Figure 3.2 outlines each section of Subpart BB of 40 CFR 60.

FIGURE 3.2
STANDARDS OF PERFORMANCE
KRAFT PULP MILLS

A7568		Standards of Performance for Kraft Pulp Mills February 23, 1978 Subpart BB
p.7572	60.280	Applicability and Designation of Affected Facility
p.7572	60.281	Definitions
p.7573	60.282	Standard for Particulatre Matter
p.7573	60.283	Standard for Total Reduced Sulfure (TRS)
p.7573	60.284	Monitoring of Emissions and Operations
p.7574	60.285	Test Methods and Procedures

Within the Subpart of the Regulations, an affected source can determine which facilities within that source are regulated, the pollutants that are regulated, emission limits, monitoring requirements and reporting requirements. For Subpart BB, Standards of Performance for Kraft pulp mills, the pollutant regulated, its emission limit and monitoring requirements are indicated in Table 3.6. Under NSPS for Kraft pulp mills, total reduced sulfur (TRS) emissions are monitored for operation and maintenance purposes. Compliance with the emission standard is determined by Federal Reference Method 16 or 16A.

TABLE 3.6
SUBPART BB, STANDARDS OF PERFORMANCE FOR KRAFT PULP MILLS
POLLUTANT MONITORING REQUIREMENTS

Source Category	Affected Facility	Pollutant	Emission Limit	Monitoring Requirement
Subpart BB - Kraft Pulp Mills				
Proposed/effective 9/24/76 (41 FR 42012)	Recovery furnace	Particulate	0.044 gr/dscf (0.10 g/dscm) corrected to 8% oxygen	No requirement
Promulgated 2/23/78 (43 FR 7568)		Opacity	35%	Continuous
Revised 8/7/78 (43 FR 34784)		TRS (a) straight recovery	5 ppm by volume corrected to 8% oxygen	Continuous
		(b) cross recovery	25 ppm by volume corrected to 8% oxygen	
	Smelt dissolving tank	Particulate	0.2 lb/ton (0.1 g/kg)BLS	No requirement
		TRS	0.0168 lb/ton (0.0084 g/kg)BLS	No requirement
	Lime kiln	Particulate (a) gaseous fuel	0.067 gr/dscf (0.15 g/dscm) corrected to 10% oxygen	No requirement
		(b) liquid fuel	0.13 gr/dscf (0.30 g/dscm) corrected to 10% oxygen	No requirement
		TRS	8 ppm by volume corrected to 10% oxygen	Continuous
	Digester, brown stack washer, evaporator, oxidation, or stripper systems	TRS	5 ppm by volume corrected to 10% oxygen	Continuous
			*exceptions; see standards	Effluent gas incineration temperature; scrubber liquid supply pressure and gas stream pressure loss

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Concurrent with the continuous emission monitoring requirement are parameter monitoring requirements within the Kraft pulp mill facility. Table 3.7 reflects those affected facilities requiring parameter monitoring.

TABLE 3.7
PARAMETER MONITORING REQUIREMENTS
KRAFT PULP MILLS

Affected Facility	Parameter Monitored
Point of incineration of effluent gases from digester, brown stock washer, multiple-effect evaporator system, black liquor oxidation system or condensate stripper system	Combustion temperature
Lime kiln or smelt dissolving tank using a scrubber emission control device	Pressure loss of gas stream through control equipment Scrubber liquid supply pressure to control equipment

4.0 CONTROL AGENCY CEM INSPECTION PROGRAM

4.1 INTRODUCTION

The Clean Air Act was the Nation's first Federal enforceable law designed to protect the health and welfare of the population from airborne pollutants. More importantly, sections within the Clean Air Act provided the U.S. Environmental Protection Agency authority to (1) implement a research and development program and (2) to provide technical assistance to State and Local Governments in the execution and implementation of enforcing the provisions of the Act in controlling air pollution from affected sources. The Act recognizes the primary responsibility in prevention and control of air pollutant lies with the state. Congress feels that each state contains a unique inventory of sources and consequently, each state should have the primary responsibility for designing and operating a control program to achieve the pollutant reduction necessary to meet the national ambient standards. The Act recognizes the need for an effective, cooperative and coordinated effort between the Federal, State and local agencies to carry out its provisions. It is the ultimate responsibility of the Federal Government to promote the "public health and welfare and the productive capacity of its population." This cooperation between Federal, State and local agencies is structured through the EPA's stationary source compliance program. The program was initiated to determine a source's compliance status with CEM regulations.

The stationary source compliance program addresses pollutants regulated in three sections of the Clean Air Act.

- o Section 110 - State-adopted, EPA-approved State Implementation Plan (SIP) requirements to meet the National Ambient Air Quality Standards for seven criteria pollutants;
- o Section 111- Implementation of emission controls to establish uniform, technology-based national emission standards for categories of affected new sources. These requirements are known as New Source Performance Standards (NSPS). These standards are Federally promulgated and are usually delegated to state authority.
- o Section 112 - Hazardous air pollutant standards for certain souce categories of asbestos, beryllium, mercury, and vinyl chloride. The National Emission Standards for Hazardous Air Pollutants (NESHAPS) are also Federally promulgated and are usually delegated to State authority.

4.2 CONTROL AGENCY COMPLIANCE PROGRAM

Control agency CEM inspection programs have used CEM certification activities and periodic on-site inspection as a tool to determine a source's compliance status. The regulatory agency CEM certification activities involve initial application, agency review and CEM certification of installed monitoring systems. The on-site inspection involves records review, control equipment evaluation, evaluation of installed continuous emission monitors through selective audits or Performance Specification Testing (PST). Each of these techniques was designed to provide the inspector with information so a determination of continued compliance can be made of the continuous emission monitoring system.

Historically, stack testing has been used as part of a source's initial compliance determination. As NSPS standards developed, continuous emission monitors became a part of regulatory agency's compliance program for those sources required to monitor their emissions on a continuous basis. Historically, CEMs have played a limited role in this program. Even with the 1975 promulgated regulations requiring CEMs as a means of monitoring a source's "continuous compliance" status, it has taken 10 years to identify CEM data as an enforcement tool and bring it to national attention. This lack of use may be attributed to early monitor problems associated with reliability, accuracy and long term performance. However, many of these earlier problems have been resolved. Consequently, such data has become a valuable source of information by which regulatory agencies can base their enforcment decisions. Regulatory agencies have increased their reliance upon CEM data in its compliance and surveillance programs. Eventually, CEMs will become part of all NSPS and NESHAPS standards as they become promulgated or revised, if a compliance method is specified.

Sources subject to the requirements of using CEMs as a compliance determination are generally required to submit to regulatory agencies quarterly excess emission reports (EER's). The EER contains information on number of excess emission over a standard, time and duration of those incidences, reason codes for those incidencies and corrective/preventive action taken to reduce those incidences. As personnel and funding limits the feasibility of on-site inspections, the EER becomes an important "feedback" system for both the source and the regulatory agency. The EER becomes a tracking tool by which agency personnel can evaluate both the control equipment and CEM performance.

In recent years, the EER report has not only been used to report excess emissions, but also other information associated with both control equipment and monitor performance, such as:

- excess drift determinations;
- quarterly audit results;
- relative accuracy tests;
- average control device parameters (pressure drop, milliamps, flow rates, etc.);
- "out-of-control" situations; and
- control equipment "baseline" information.

With limited control agency resources and manpower, the EER is the "tracking" mechanism for monitor and control equipment performance during periods when the agency personnel are unable to perform on-site evaluations, as part of the "continuous compliance" strategy.

Knowing that the purpose and scope of agency inspections vary with manpower, a three phase and four level compliance inspection program has been developed by the State of Pennsylvania Department of Environmental Regulations and is presented below as an example of a successful program. Each inspection phase or level is dependent upon the other for proper information and determination.

The phase process consists of administrative activities involved with initial CEM system application, performance testing and final approval. This enables the state or federal agency agency to approve the monitoring system through established certification procedures. The type of activities at each phase are:

> Phase I - Initial approval of CEM application as required through source permit, by the regulatory agency;
>
> Phase II - Observation of performance specification testing (PST) of the installed CEM system; and
>
> Phase III - Review of the PST report, with final approval or disapproval.

The level approach begins after completion of the phase evaluation. The levels of CEM inspection extend from source agency records review (lowest level) to stack test compliance determination (highest level). The intensity and thoroughness of the inspection increases numerically. The primary objective of an agency on-site inspection and excess emission review is to minimize air pollution through adherence to regulations and permit stipulations. The inspection provides the determination or confirmation of compliance and helps identify causes of excess emissions. The types of activities at each level of the CEM system inspection are:

> Level I - Records review involving excess emission reports, previous inspection reports, source "working" file review and permit review;
>
> Level II - On-site inspection involving review of monitor recordkeeping (maintenance, monitor and control equipment logs), monitor fault light indicator review, monitor internal zero/span check, strip chart review and electronic checks;
>
> Level III - Evaluation of installed CEMs through external audit techniques involving neutral density filters for opacity monitors and gas cylinders/cells for gas monitors; and
>
> Level IV - Comparative evaluation of installed CEMs through performance testing utilizing Federal Reference Methods or portable CEMs.

The purpose of the increasing level of inspections is to concentrate the resources of the control agency personnel on those facilities that have the greatest potential to exceed the emission limits.

The phase and level audit procedures have been designed so that each activity indicates whether or not the CEM system has achieved the necessary level of compliance before starting the next phase. For example, if the agency records audit reveals that the PST has not been successfully completed, the agency may request that this be done before continuing with the remaining phases. In this case, EERs might otherwise be reviewed assuming invalid data, precluding any enforcement action based upon emission rate data contained in the reports. Since the CEM data may be assumed to be invalid, the source records audit may not be worthwhile.

The phase and level audit procedures are described in greater detail below and outlined in checklist format, as a Supplement to this manual entitled: " Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills- Evaluation Procedures."

4.3 CONTROL AGENCY ADMINISTRATIVE REVIEW ACTIVITIES - PHASE I, II, III

4.3.1 Phase I - Regulatory Review of Source Application/Permit

Phase I involves the initial application of the source to the regulatory agency describing the total CEM program. The application is a response to permit requirements as regulated by regulatory authorities. The permit becomes the guideline for implementation of the CEM Program.

The permit is part of four major control strategies in an agency enforcement system. These strategies are:

- permit to construct and install operation;
- permit for continuous operation;
- compliance enforcement; and/or
- surveillance and complaint response;

The main objective of the permit regulation is to control emissions from new or modified sources so those emissions do not:

- violate National Ambient Air Quality Standards (NAAQS);
- cause significant deterioration to prevent attainment or maintenance of the NAAQS; and
- result in violations of the applicable portions of existing control strategy.

As required by the Clean Air Act, all states must have an established permit systems as part of their federally approved State Implementation Plan. Permits may be administered either by local, state and/or federal agencies depending upon who maintains regulatory authority over the industry. Usually all major emitting facilities are included in state and local permit regulations. Section 110d of the 1970 Clean Air Act defines a major emitting facility as any stationary facility or source which directly emits, or has a potential to emit, one hundred tons per year or more of any regulated pollutant.

As part of the 1977 CAA Amendments, the federal government was given the added responsibility of reviewing all permits for major sources constructing in Prevention of Significant Deterioration (PSD) and nonattainment areas. Federal review applied to:

- PSD areas for any source having a potential emission greater than 250 tons per year or 100 tons per year for 28 specified sources; and
- nonattainment areas for any source which have a potential emission greater than 100 tons per year.

The permit, therefore, is an integral part of an agency enforcement program. It provides the vehicle by which agency CEM objectives become implemented and enforceable. The permit aids both the regulatory agency and the applicant by:

- providing engineering review prior to construction so any necessary changes can be made at the lowest cost;
- if proposed facility cannot comply with emission limitations, then agency can prevent construction;
- agency can require basic quality assurances activities and proper operative procedures implementations into the permit to insure continued performance of control and CEM equipment;
- deny operating permit so if source does not meet compliance limitations, then source cannot operate;
- provides a format for notification of source modification; and
- provides a "document" in which all conditions/specifications to operate are stated.

The permit also provides guidelines to the source as to control agency CEM program and objectives. It is within the permit that the control agency can ensure that an established CEM program exists at the source that it can meet all regulatory requirements. The permit not only addresses the operating conditions of the source, but also the total continuous emission monitoring system.

The permit should include, at a minimum, four major areas of information associated with the continuous emission monitoring system. They are:

I. General Information;

II. Management Control System (MCS);

III. Standard Operating Procedure (SOP) Manual; and

IV. Quality Assurance (QA) Program;

4.3.1.1 General Information -

General information allows the control agency to become familiar with the process and the monitoring system used to evaluate that process. It also enables the control agency to evaluate the relationship between the process and the CEM system. With this information, the control agency can approve/disapprove the application of the CEM system for that particular source. Under the General Information section, the permit should require the following:

- General description of the process and pollution control equipment. All factors affecting that operation on maintenance of the maintainable system should be involved;
- Location of monitoring system sample acquisition point(s) in relationship to:
  - o Flow disturbance (fans, elbows, inlets, etc);
  - o Pollution control equipment;
  - o Emission point of the monitored gases; and
  - o Flow diagram illustrating location of all sampling points.
- System information, including:
  - o Operating principle of the pollutant analyzer;
  - o Equipment manufacturer;
  - o Manufacturer's literature; and
  - o Manufacturer's claimed performance specifications.
- Process and pollution control equipment operating parameters which affect the emission levels of the pollutant(s) being monitored, and a description of the method to be used to record significant parameters.

4.3.1.2 Management Control System (MCS) -

Documentation associated with the Management Control System (MCS) enables the agency to track who is responsible for the CEM system. It assigns individual management of each subsection. The MCS outlines administrative procedures applicable to all management systems and assigns responsibility for all phases of the CEM system operation.

4.3.1.3 Standard Operating Procedure (SOP) Manual -

The SOP manual should be a document defining all activities, responsibilities, communication loops, documentation procedures, flow charts for data acquisition/data handling, trouble shooting guides and preventive management task/schedules. Calibration procedures, including acceptance limit for monitor performance, should be specified. Table 4.1 illustrates the different sections of a typical SOP manual.

TABLE 4.1
STANDARD OPERATION PROCEDURE MANUAL
(Typical Outline)

- Section 1. Introduction
  - 1.1 Standard Operational Procedure Manual Description and Format
  - 1.2 References
- Section 2. Quality Assurance Objectives
  - 2.1 General
  - 2.2 Specific
- Section 3. Organization
  - 3.1 Personnel Assignments and Responsibilities
    - 3.1.1 Organization
    - 3.1.2 Program Management
    - 3.1.3 Field Operations
    - 3.1.4 Laboratory Operations
    - 3.1.5 Data Management
  - 3.2 QA Responsibilities
    - 3.2.1 Quality Assurance Coordinator
    - 3.2.2 Field Personnel
- Section 4. System Operation
  - 4.1 Monitoring Site Description
  - 4.2 Start-up Procedures
  - 4.3 System Check-out
  - 4.4 System Operation
  - 4.5 Computer System Troubleshooting
  - 4.6 Software Documentation
  - 4.7 Routine Operating Procedures Checklist
- Section 5. Principles of Operation
  - 5.1 General
  - 5.2 Calibration Modes
  - 5.3 Computer Control Subsystems
  - 5.4 Monitor Subsystems
- Section 6. Quality Assurance
  - 6.2 Performance Audit Procedures and Checklist
  - 6.1 System Audit and Checklists
- Section 7. Documentation
  - 7.1 Monitoring
  - 7.2 Daily Log Book
  - 7.3 Maintenance and Troubleshooting Log Book
- Section 8. Data handling, Validation and Reporting
  - 8.1 Data Logistics
  - 8.2 Data Handling and Statistical Analysis
    - 8.1.1 Quality Control of Data Handling
    - 8.2.2 Calculations
    - 8.2.3 Statistical Evaluation
  - 8.3 Control Charts
  - 8.4 Data Validation Criteria
  - 8.5 Data Reporting
  - 8.6 Data Forms
- Section 9. Maintenance
  - 9.1 General
  - 9.2 Preventive Maintenance
  - 9.3 Corrective Maintenance
  - 9.4 Spare Parts Inventory
  - 9.5 Maintenance Documentation

4.3.1.4 Quality Assurance Program -

The main objective for requiring a quality assurance (QA) program for the installed CEM is to insure that all data collected and reported is meaningful, precise and accurate within a stated acceptance criteria. The program should be strong enough to insure strict adherence to all established procedural requirements, but flexible enough to allow continuing evaluation of its adequacy and effectiveness. Once a QA plan is written and implemented, assessment procedures within the plan should point out any necessary corrective action which, in effect, revises the plan.

The QA program should involve two major divisions:

- Quality Assurance - activities to address the necessary status and reliability of the installed CEM system; and
- Quality Control - functions initiated when quality assurance indicates data reliability outside predetermined control limits.

Both of these topics will be discussed further in Chapter 11, Quality Assurance/Quality Control.

4.3.2 Phase II - Performance Testing of Installed Continuous Emission Monitoring System

After the approval by the regulatory agency of Phase I, the industry proceeds with the purchasing, installation and performance testing of the CEM system. Activities for the regulatory agency during Phase II involve receiving notification (in 30 days) from the source of pending Performance Specification Testing of permitted CEM system, observing the testing during the PST and reviewing results.

4.3.3 Phase III - Regulatory Approval of Installed Continuous Emission Monitoring System

Phase III, Final Approval, consists of reviewing the Performance Test report. All information required to be gathered during Phase II must be reported according to the following specifications:

A. For opacity monitors, 40 CFR 60, Appendix B, Performance Specification Test 1;

B. For total reduced sulfur (TRS) monitors, 40 CFR 60, Appendix B, Performance Specifications Test 5; and

C. For oxygen and carbon dioxide monitors, 40 CFR 60, Appendix B, Performance Specification Test 3.

The reviewer should make a determination of the acceptability of the test results and procedures. This determination should support a final approval, or disapproval of the CEM system.

Other activities associated with Phase III involves necessary source recordkeeping and reporting requirements to the regulatory agency. The agency specifies what records are to be maintained and what is to be reported.

4.4 CONTROL AGENCY CEM INSPECTION REVIEW ACTIVITIES - LEVEL I, II, III, and IV

Level I, II, III, and IV CEM inspection review activities involve records review, agency records update, source records review and onsite inspection. The control agency can make a preliminary determination of the CEM program compliance status at a given source, without travel or significant time expenditure, through a record review. From the EER and PST reports, compliance status with installation, testing, and notification requirements can be ascertained. The on-site review involves maintenance records review and sources process and control system CEM records review. From this information, the agency can determine the status of the CEM system and whether it is being maintained. If the source record review indicates weaknesses, the inspector can proceed to on-site evaluation of installed continuous emission monitors utilizing external audit techniques.

The purpose of a field inspection is to, therefore, verify first hand the information already obtained or requested through the records review. The inspection is especially worthwhile when the source has not demonstrated compliance with the installation, testing, notification, and recordkeeping regulations, or when the earlier audit results do not clearly identify the CEM compliance status. The field inspection may also be used when conducting a plant inspection or observing an emissions performance test.

Consequently, the on-site inspection involving Levels I, II, III and IV provides a complete CEM system evaluation, from records review to performance testing.

4.4.1 Control Agency Records Review - Level I

Level I CEM inspection procedures involves a "thorough" working knowledge of the facility from information gathered through file review. Level I inspection is routine file review and administrative, intended to identify problem areas without attempting to solve them. The process involves review of information found in the source's:

- Facility "permanent" file; and
- Facility "working" file.

The facility "permanent" file contains basic information associated with the application and certification of the continuous emission monitoring system. This would involve:

- Original permit;
- Compliance schedule and variance;
- CEM certification report; and
- Final permit approval documentation.

A review of the available background information on the facility to be inspected is essential. This review will enable the inspector to become familiar with the facility's process and emission characteristics.

The following types of information should be reviewed as part of the "permanent" file:

4.4.1.1 Basic Facility Information -

- Names, titles, and phone numbers of facility representatives;
- Maps showing facility location and geographic relationship to residences potentially impacted by source emissions;
- Process and production information; and
- Flowsheets identifying sources, control devices, monitors, and other points of interest.

4.4.1.2 Pollution Control Equipment and Other Relevant Equipment Data -

- Description and design data for control devices and relevant process equipment;
- Sources and characterization of emissions;
- Continuous emission monitoring system(s) data; and
- Baseline performance data from both control equipment and continuous emission monitors taken during certification.

4.4.1.3 Regulations, Reporting Requirements, and Limitations -

- Most recent permits for facility sources;
- Compliance schedule and variances;
- Applicable Federal, State, and local regulations and reporting requirements;
- Any required periodic reporting;
- Special exemptions and waivers, if any;
- Acceptable operating conditions for control equipment and continuous emission monitors; and
- Continuous emission monitor certification reports.

Once the inspector has become familiar with the "permanent" file, he should then review the source's "working" file.

The "working" file should contain basic information associated with the facility compliance and enforcement history. In particular, the review of the source's "working" file should include:

- Previous inspection reports;
- Compliance history including reports, follow-up, findings and remedial action; and
- Quarterly excess emission reports (EERs).

4.4.1.3.1 Previous Inspection Reports -

Review of previous inspection reports allows the inspector to become familiar with chronic problems associated with the control equipment or the continuous emission monitoring system. It allows him to "baseline" both the pollution control equipment and the continuous emission monitoring system. The fundamental principle underlying the baseline approach is that both control equipment and continuous emission monitors are evaluated by comparison at present conditions with machine/monitor specific baseline data. Their operating characteristics and performance levels are unique. By comparing previous inspection reports with initial compliance observation data, the inspector is able to identify potential source related problems.

4.4.1.3.2 Compliance History -

Compliance history review enables the inspector to identify control equipment problems and possible continuous emission monitor malfuncitons.

4.4.1.3.3 Excess Emission Reports -

The most important review as part of level 1 "working" file is the review of the source's excess emission reports.

EPA has promulgated regulations requiring certain NSPS facilities to install, maintain, and operate continuous emission monitoring systems. In addition, EPA has required that State Implementation Plans (SIPs) be revised to require certain existing facilities to install, maintain, and operate CEM systems. These regulations require "performance testing" and "periodic reports and recordkeeping of the nature and magnitude of such emissions." Furthermore, Sections 113 and 114 of the Clean Air Act (CAA), as amended in 1977, require the use of recordkeeping and reporting requirements as means of enforcing emission standards.

Historically, the reporting requirements for NSPS sources (40 CFR Part 60) have involved a written report for any calendar quarter in which source emissions exceed the value of the standard. The emission value, as recorded by the CEM system (i.e., % opacity, ppm, lb/ton, etc.) must be recorded, as well as the duration (i.e., six minutes, 12 hours, etc.) of the excess emission. An excess emission is defined as exceedance of the emission limit values over the time period specified by the subject standard. Similiarly, 40 CFR Part 51 requires some existing stationary sources to implement a continuous monitoring program and to provide quarterly excess emission reports (EERs). The minimum information required in the excess emission report is:

- The magnitude, duration and date of excess emissions;
- The identification of each excess attributable to start-ups, shutdowns, and malfunctions;
- The cause of any malfunction and the corrective action or preventive measures adopted to the system;
- The date, time, and duration of any monitor outage for reasons other than zero and span checks;

- The reason for monitor outage and corrective action taken; and
- Statement of no excess emissions and/or monitor outages, if applicable.

Excess emission reports are reviewed in three levels. The three levels are:

- Level 1 - Initial review and summary of the CEM data;
- Level 2 - Confirmation of Level 1 results, targeting of sources for follow-up, and data input to the CEMs subset of the Compliance Data System (CDS); and
- Level 3 - Follow-up comparison of CEMs data and other emission data with potential recommendations for additional testing or compliance/enforcement action.

To assist the inspection in evaluating previous EERs, a standardized form has been recommended by EPA and is found in Section 10.0 of this manual.

Once the "permanent" and "working" files have been reviewed, the inspector should have a good idea of the present operation and maintenance practices of the control equipment, the continuous emission monitoring system and the compliance status of the source. He is now ready to proceed to Level II to verify his findings from the records review (Level I).

4.4.2 - Source Records and Continuous Emission Monitoring System Review - Level II

Level II involves a "walk through" inspection of the regulated facility. The on-site "walk through" inspection is the foundation for a control agency compliance monitoring strategy and enforcement programs. The on-site inspection provides:

- Compliance data to determine or confirm source compliance with the regulations;
- Information on identification of violations;
- Base for establishing an enforcement action through documentation;
- promoting agency's continuous compliance strategy; and
- informal consulting to assist facility in identifying and resolving compliance problems.

A Level II inspection is a detailed evaluation of all aspects of the continuous emission monitoring system. This involves review of recordkeeping and reporting activities, strip chart/data processor review, CEM daily zero/span checks, remote display review, and control equipment review. In essence, the control agency inspector is correlating information from the Level I review and comparing it to the on-site inspection.

An inspection of the CEM system includes a general evaluation of the CEM sample interface and reference method sample locations for gaseous systems and evaluation of the representativeness of the optical pathlength of transmissometers. These evaluations can only verify whether or not the general location criteria are met, and if additional stratification (gases) or particulate distribution (opacity) evaluations are needed. This should have been addressed prior to actual installation and testing; however, the subject of CEM location is often overlooked, especially for systems installed several years ago.

The field inspection of the CEM installation offers an opportunity to evaluate environmental aspects such as temperature, vibration, and other variables which often have a direct bearing on monitor reliability. When gases are analyzed using extractive monitors located remotely from the sample interface, the sample and calibration gas transport systems can be inspected. Heat tracing, insulation, weather protection, transport line, and connection material should be evaluated. For analyzers measuring "wet" gas concentrations, gas temperature must be maintained above the dew point.

Conditioning systems are an integral part of any TRS CEM system. It is essential for extractive monitors that all moisture and particulate matter be removed from the sample prior to the analyzer to eliminate interference and to avoid corrosion in the analyzer. The conditioning system should be properly designed and maintained, to avoid system malfunctions, which can cause reduced monitor availability and preclude data validation.

By actually inspecting the analyzer location, the auditor develops an appreciation of its accessibility for maintenance. Maintenance accessibility may have been compromised in achieving a representative location with an environment suitable for operation. When reviewing future monitor malfunctions in EERs, this information can be pertinent to the evaluation of malfunction duration.

Calibration gas cylinder location should be reviewed. If the cylinders are exposed to ambient temperatures, some assurance of proper cylinder material selection to insure thermal stability is recommended. This can be provided from the gas supplier as part of the purchase agreement, although at some additional cost. The location and pressure of the calibration gas interface with the sample system should be verified.

The inspector should check the calibration while on-site to document procedures, calibration reference values, and provide a spontaneous quality assurance check. Familiarity with the system output during a calibration will aid in future review of data submitted to the agency in EERs and any other reports.

Reference material certification documentation such as gas traceability or triplicate analysis should be available in plant records and verified during the field inspection.

The analyzer and/or control unit should be inspected to assure that zero compensation limits have not been exceeded and fault indicators not illuminated. The control unit and recorder output should be visible to operators to assure their awareness of malfunctions. An alarm pickup from the control unit to annunciate excess emissions is an appropriate means of expediting operator response to reduce emissions, when necessary.

A discussion between the inspector and those operators responsible for acknowledging excess emissions and monitor malfunctions is recommended to stress the use of the monitor output to initiate corrective action for these situations. It is also necessary to inspect the records documenting these events to ensure that acknowledgement of excess emissions, indicated by the CEM, and that corrective action by the plant operator has occurred within a reasonable response time has taken place. Plant O&M records should be reviewed to insure that both the CEM process and control equipment maintenance is properly documented and corresponds to recorded excess emissions events and monitor malfunctions.

A similar review of data reduction calculations for conversion to emission rates to verify conversion factors and formulas is necessary. When automated computation is utilized, these conversion procedures should be periodically reviewed to be certain of accuracy. This can be done by the source and agency when preparing and reviewing quarterly EERs.

To ensure that all information is obtained in order to make a proper decision, the inspection should be performed in an organized and coherent fashion. To accomplish this, the counter flow approach is utilized. The counter flow approach is so named because inspection is accomplished counter to the flow of information from the continuous emission monitoring system. Figure 4.1 illustrates the counter flow technique.

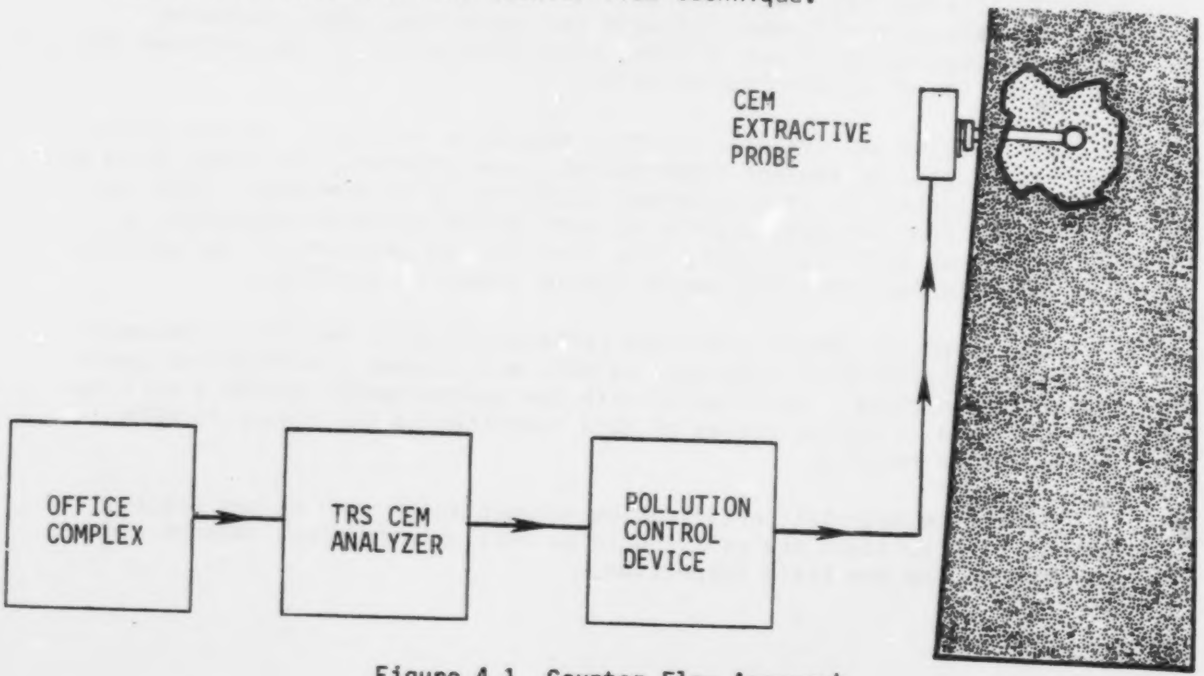

Figure 4.1 Counter Flow Approach

The counter flow technique is most applicable for inspecting facilities where baseline data is available. At each location, the inspector should compare existing data to baseline data to determine degree of compliance.

4.4.2.1 Office Complex -

The Level II inspection begins at the office complex. All personnel involved in the inspection should gather in a room for the opening conference. The purpose of the opening conference is to inform facility official(s) of the purpose of the inspection, the authority under which it will be constructed, and the procedure to be followed. The opening conference also offers the inspector the opportunity to strengthen agency-industry relations through a positive attitude and provide relevant information and other assistance. The effective execution of the opening conference on the inspector's part often "sets the tone" for the remainder of the inspection.

During the opening conference, the inspector should cover the following items:

- Inspection Objectives - An outline of inspection objectives will inform facility officials of the purpose and scope of the inspection and may help avoid misunderstandings;
- Inspection Agenda - Discussion of the sequence and content of the inspection, involving the continuous emission monitoring system operations and control equipment and its current operating status, should be discussed. This will help eliminate wasted time by allowing facility officials time to make any preparations necessary. The types of measurements to be made and the samples to be collected (if any) should also be addressed;
- Facility Information Verification - The inspector should verify or collect the following information:
    - Correct name and address of facility;
    - Correct names of plant management and officials;
    - Principal product(s) and production rates;
    - Sources of emissions; and
    - Locations of emission points.
- Records Review - A list of records to be inspected should be presented. This will allow company officials time to assemble needed documentation. Needed records for review are:
    - previous quarter excess emission reports (EERs);
    - source log books;
        - o CEM operation log book;

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  - o Control equipment log book;
  - o CEM maintenance log book;
- strip charts for previous quarter or computer print-outs; and
- source permit or variance information.

- Safety Requirements - The inspector should determine what facility safety regulations including safety equipment requirements will be involved in the inspection and should be prepared to meet these requirements. The inspector should also inquire about emergency warning signals and procedures;

- Inspection Schedule - A timetable associated with the inspection will allow plant personnel to consider lunch, breaks and quitting times;

- Inspection - Discuss with plant personnel the techniques of inspection, the objective of performing the inspection, etc.;

- Closing Conference - A post-inspection meeting should be scheduled with the appropriate officials to provide a final opportunity to gather information, answer questions, perform calculations and make recommendations. At this time the inspector should discuss any new rules and regulations that might affect the facility and answer questions pertaining to them. If the inspector is aware of proposed rules that might affect the facility, he or she may wish to encourage facility officials to obtain a copy.

Once the opening conference is concluded, the inspector should begin reviewing source documentation associated with the continuous emission monitoring system.

The main objectives of document review is to cross-correlate information from one source to another. For example, if the strip chart/data logger indicates an excess emission, has it been properly documented in the excess emission quarterly reports? Likewise, if the strip charts indicate no emission for a time period, does this correlate with plant log books or CEM maintenance log books? Strip charts should be reviewed for consistency of daily zero/span checks, properly noted with date, time, etc., and reviewed for normal/abnormal emissions. In general, data inspection involves:

- compliance with recordkeeping and reporting requirements of the permit;

- checking records for data validation and proper data reduction procedures;

- reviewing strip charts/data logger for consistency with zero/span values, excess emissions, proper notation, etc.; and

- review of all maintenance logs for proper entries;

After an extensive review of the records, the inspection proceeds to the continuous emission monitoring equipment. Historically, the CEM system involves five major components:

- Data recorder/data processor;
- Analyzer;
- Calibration system;
- Sample conditioning system; and
- Probe/extraction system.

4.4.2.2 Control Room -

4.4.2.2.1 Data Recorder/Data Processor -

There are many kinds of data output and recording devices which can be attached to the monitoring equipment. Except for checking the zero and calibration adjustments daily, there is no requirement for any visual display of the monitor output. Data may be recorded in any manner which allows the source to reliably and accurately maintain the files required by the regulations. As a minimum, each analyzer unit in the system must produce an output signal showing instantaneous pollutant concentration. When recorded on a strip chart recorder, this signal represents an emission versus time record which may be manually or mechanically integrated to provide the various emission averages required by the regulations.

At the source's option, these signals may be wired directly into various integrating modules, computing devices, or data loggers, which produce the required averages directly as their output. This information is then stored on some storage media, or send it to a computer for further analysis. Regardless of how this is done, these recorded values may be combined with additional factors (calibration and conversion factors, zero and span corrections, oxygen correction, etc.) to yield the emission records required by the regulations.

The inspection of the data processor therefore may involve certifying that this conversion is performed properly. Additionally, the data processor may be a source of information concerning routine maintenance practices and monitor malfunctions. The strip chart or data logger recorder should be checked to insure that a good record is being produced from the analyzer output. The total data processing system should be checked for reliability and accuracy.

4.4.2.2.2 Analyzer -

The analyzer inspection involves noting present operating status of the analyzer. Various gauges/regulators and valves should be inspected for proper setting and operation. These settings should be referenced back to the initial baseline data. Emissions, as displayed by instrument meter, should be compared to the data processor to insure proper notation. Additionally, any fault light indicators should be noted and recorded on the field inspection form. At this time, an internal zero/span check should be performed. When the checks are made, note the resulting zero and span readings. The values or changes in values from the previous routine check should be consistent with the changes recorded in the maintenance records. Finally, the internal zero/ span calibration check should be within the performance specification guidelines.

4.4.2.2.3 Calibration System -

In addition to zero/span verification, the inspector should examine the calibration system and gases used to generate the zero/span values. Regulations require that the gases be EPA Protocol 1, or NBS traceable or analyzed by the Federal Reference methods every six months. The inspector should verify the procedure of certification and assigned concentration. The value should be consistent with the value recorded in the data processor unit or monitor log book. Additionally, the inspector should verify that the daily zero/span checks evaluate the monitoring system in total. This includes all components: the conditioning/extraction system, the analyzer system and the data acquisition system. In some types of monitoring systems, however, certain instrument components are bypassed during calibration checks. For instance, in certain types of monitors, calibration is performed only in the electronics. The inspector should, therefore, attempt to find out how the unit actually performs the calibration. Does the procedure check the entire system or not? If not, the personnel at the source should be asked how they check the rest of the monitoring system.

4.4.2.3 Control Device

The purpose of inspecting the control equipment is to determine if the unit is operating according to manufacturer guidelines and within limits determined during the Performance Specification Test. In essence, the inspector is comparing the present operation of the control device to its individual operating specifications. These specifications values are "baseline" values by which the inspector can reference to the on-going inspection. If a particular indicator of the operation of the control equipment (milliamps, scrubber pH, primary/secondary current) changes from the baseline value, then this becomes a possible indicator of deteriorating operation. The inspector is looking for possible deviation from baseline operating conditions and relating these deviations to operating/maintenance practices. The malfunction of the control equipment may cause violations or noncompliance with permit emission limitations.

Consequently, baselining the control equipment is very important in a control agency continuous emission monitoring program. Baselining the control equipment helps in the evaluation of the continuous emission monitoring system on the source. Baselining the control equipment can be performed:

- After initial operation and during normal plant process;
- During stack test to establish representative operating conditions;
- During initial compliance test for NSPS sources;
- During Performance Specification Testing; and
- During each source inspection visit to establish normalized operating parameters.

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Baseline information also allows the inspector to note changes from manufacturer stated values, evaluate the direction and magnitude of those changes and determine long-term performance of the control equipment. More importantly, it allows him to re-evaluate his inspection schedule and update routine inspections or compliance testing.

4.4.2.4 CEM Interface System -

4.4.2.4.1 Sample Conditioning System -

The sample conditioning system usually involves removal of interfering species from the gas stream which would affect the detector system. This may involve particulate matter, moisture and SO_2 removal. Heat trace lines should be operating to maintain temperature of sample gas from conditioning system to analyzer. Inspection points are more visual than action oriented. The inspector should insure that valves are operating, the transfer line is heating, the moisture removal system working, etc.

4.4.2.4.2 Probe/Extraction System -

Inspection of the probe/extraction system may be performed by observing through an additional porthole opposite the system. The inspector should determine if certain problems exist such as: probe plugging, vibrational problems, temperature problems, or moisture problems in the extraction system.

Once the inspector has inspected the probe/extraction system, he has completed the visual inspections of the system. He should then proceed back to the conference room to compare notes and initiate the closing conference.

4.4.2.5 Closing Conference -

The closing conference enables the inspector to "close-out" the inspection including answering questions from plant personnel. The closing conference enables both the inspector and industry representative to evaluate the inspection. For the inspector, it enables him to collect missing data needed to complete the evaluation. In general, the following should be covered in the closing conference:

- Review of Inspection Data - All information gathered during the inspection should be reviewed for completeness. Any missing data or requested data should be exchanged at this time.
- Inspection Discussion - All questions relating to the inspection should be answered at this time. However, caution should be taken by the inspector in answering questions relating to compliance status or enforcement action as a result of the inspection.
- Recommendations - At this time, the inspector can make recommendations as to possible solutions to deficiencies noted during the inspection. The inspector should suggest available technical publications or documents relating to the continuous emission monitoring system which would address the noted deficiencies.

To assist the inspector in performing all functions associated with Level I and II of the Control Agency Inspection Program, a step-by-step inspection manual has been developed. The objective of this manual is to provide documentation and guidance to the inspector so he can determine if the continuous emission monitoring system is operating according to permit conditions. This document, Field Inspection Notebook for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills, is provided as a supplement to this manual.

4.4.3 - Continuous Emission Monitoring System Calibration Error Determination - Level III

The Level III inspection, for the control agency inspector, is the most costly and labor intensive. The Level III inspection becomes necessary only if the Level II inspection indicates deficiencies in the CEM system. The Level III inspection involves a complete evaluation of the monitoring system through a dynamic calibration procedure. Multiple concentration gases are injected, as close to the probe tip as possible, and the monitor response is compared to the certified gas values. From this evaluation, a calibration error is determined. If the error falls outside calibration drift performance specification values, then the monitoring system is "out-of-control". This would initiate some form of corrective action by the source or a Level IV evaluation by the regulatory agency.

Chapter 11.0, Quality Assurance/Quality Control, reviews several field calibration systems which have been used by control agency inspectors as a Level III audit system. The systems involve both permeation tube and gas cylinder techniques. These audit devices should be part of a CEM inspection program.

4.4.4 - Source Continuous Emission Monitoring System Performance Specification Re-Evaluation - Level IV

A Level IV evaluation involves a recertification of the installed CEM system utilizing Performance Specification Test 5 and 3. The role of the inspector during this Level is to observe the proper extraction and computation of emissions from the source during testing. At this time, additional "baselining" of the control equipment and continuous emission monitoring system can be performed. Inspection procedures, Performance Specification Test observation forms and report review checklists are provided in the supplement of the manual titled: "Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills-Inspection Forms."

5.0 MONITORING SYSTEM INSTRUMENTATION

5.1 INTRODUCTION

The determination of compliance with applicable standards associated with the Kraft pulp mill industry involves both opacity and gas emission limitations on a continuous basis. The monitoring system must be able to differentiate the regulated pollutant from the non-regulated pollutant.

Federal or State regulations will dictate whether an opacity monitor, gas monitor, or both are required on a given source. Many sources will be required to monitor opacity only. In such cases, instrument selection is relatively easy since there is only one measurement principle that will satisfy the EPA opacity monitor design specifications. Selection of gas monitors is more difficult since EPA has established no design specifications in this case. All that is necessary for a gaseous emission monitor to be approved is that it perform according to EPA specifications after it is installed on the source. Any chemical or physical monitoring method can be used as long as it does the job of accurately monitoring emissions (accurate, relative to the reference methods for determining pollutant gas concentration as defined in 40 CFR Part 60 Appendix A).

All categories of sources required to install continuous gaseous emission monitors are faced with the problem of selecting instruments that will give data representative of the actual source emissions. The problems that are encountered in a sulfuric acid plant will be different than those found at a primary copper smelter or Kraft pulp mill. Even within a given source category, the plant design will often dictate the choice of a monitoring system.

There are many instruments marketed for monitoring emissions from stationary sources. Opacity monitors may be either single-pass or double-pass systems. Gas monitoring systems may be either extractive systems, in-situ systems, or remote monitoring systems. These divisions are shown in Figure 5.1.

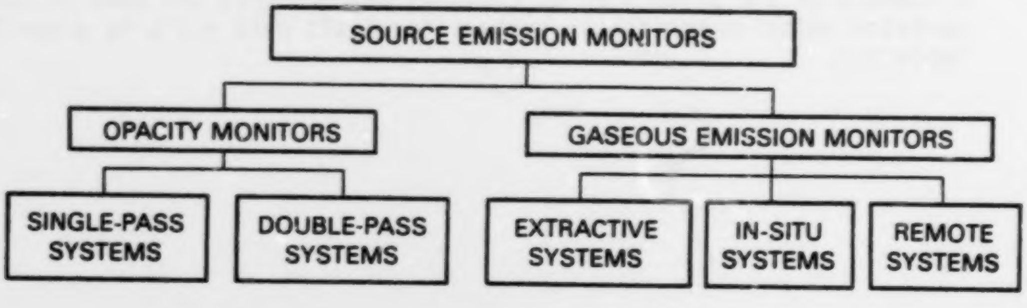

Figure 5.1. Source Emission Monitoring Systems

Extractive gas monitors were the first type of instruments to be incorporated into continuous gas monitoring systems. Many of the first extractive systems used modified ambient air analyzers or an ambient air analyzer adapted to source applications with the use of a gas dilution system. Many problems were found with this type of approach. Systems were later designed to deal directly with the problems of extracting, sampling, and analyzing pollutant gases at source level concentrations.

The extraction of a sample gas from a stack or duct presents a number of problems. To obtain accurate results, the sample must first be a representative one before entering the monitor itself. The sample must be processed by removing particulate matter, condensing water vapor, and, in some cases, removing specific gases that interfere with the analytical method. In-situ monitors on the other hand, do not require the removal of particulates or water vapor. The analysis is performed on the gas as it exists in the stack or duct, (hence, in-situ) generally by some advanced spectroscopic technique. These analyzers are either installed across a stack (cross-stack) or employ a probe inserted into the flue gas stream (in-stack). These two types of in-situ analyzers do not extract or modify the flue gas.

In-situ monitors do, however, have limitations in their application. If a stack or duct contains entrained water in the form of liquid droplets, light scattering problems and absorption of the pollutant gases in the liquid may cause the instrument values to differ from those obtained by the EPA reference method. The choice of the type of system (either extractive or in-situ) to be used in a given application will often depend upon features of the plant design and state of the art technology. The choice of a specific instrument will depend upon variables ranging from practical considerations, such as cost, to purely analytical factors, such as the scientific principle that will give the most accurate concentration data for a given pollutant. Presently, because of limitations and monitoring techniques, only extractive systems for monitoring gas emissions of TRS compounds at Kraft pulp mills are applicable.

The analytical techniques used in continuous source monitors of gaseous emissions at Kraft pulp mills encompass a wide range of chemical and physical methods. They vary from chemical methods as basic as coulometric titration to the measurement of light produced in a chemiluminescent reaction. A summary of the principles of chemical physics that are used in currently marketed emission monitoring systems for Kraft pulp mills is given in Table 5.1.

TABLE 5.1
PRINCIPLES USED IN TRS CONTINUOUS EMISSION MONITORING SYSTEMS

TRS Monitors	Diluent Monitors
Absorption Spectroscopy Methods Ultraviolet Differential Absorption	Electroanalytical Method Polarographic (O_2) Electrocatalysis (O_2) Paramagnetic (O_2)
Luminescence Methods Flame Photometry Fluorescence Spectroscopy	Absorption Spectroscopy Differential Absorption (CO_2)
Electroanalytical Methods Electrochemical Transducer Coulometric Titration	
Other Gas Chromatographic Technique Lead Acetate Optoelectronic	

The main objective of the extractive sampling system is to extract a representative sample from the source and transfer it to the detection system for analysis without compromising its integrity. If other species are present in the sample gas which interferes in the detection of the regulated pollutant, then they must be removed prior to analysis. This may involve filtering or scrubbing the gas sample before delivering it to the analyzer compartment. The gas sample is thus conditioned, refined, and analyzed. Consequently, the extraction of a gas sample from a source involves four major subsystems: (1) extraction; (2) conditioning; (3) detection and (4) recorder/data processing systems. The subsystems which compose an extractive TRS Continuous Emission Monitoring system are illustrated in Figure 5.2.

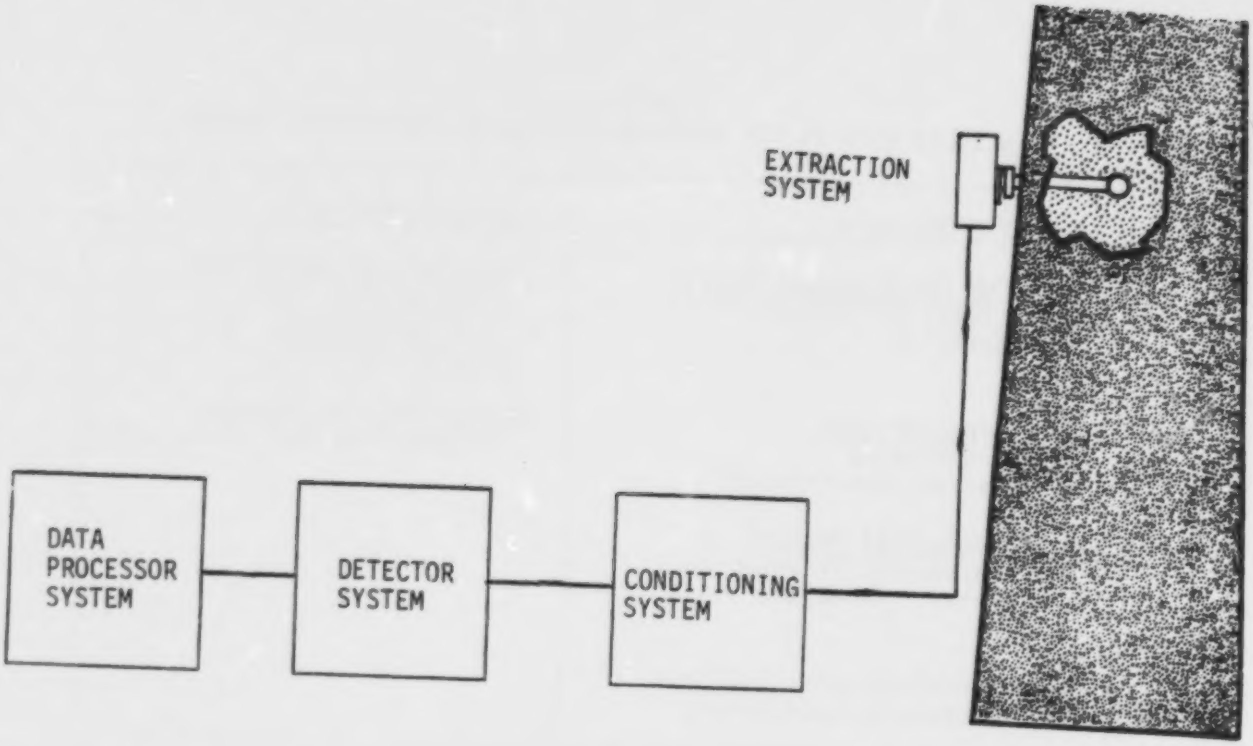
EXTRACTION SYSTEM
DATA PROCESSOR SYSTEM
DETECTOR SYSTEM
CONDITIONING SYSTEM

Figure 5.2. Subsystems of a TRS Continuous Emission Monitoring System

- Extraction System

  The purpose of the extractive system is to extract a representative sample from the source, removing particulate and moisture from the gas stream, if applicable, and transport the sample to the conditioning system;

- Conditioning System

  The conditioning system involves removal of interfering gases and other species, then oxidizing the sample (if applicable), and delivering it to the detector system;

- Detection System

  The detection system involves the measurement of the gas stream for TRS or SO_2; and

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- Recorder/Data Processor System

  The Recorder/Data Processor receives the signal from the detection system and stores/converts this information to the appropriate units.

Each system is comprised of individual components, as itemized in Table 5.2.

TABLE 5.2
SUBSYSTEM COMPONENTS OF A TRS CONTINUOUS EMISSION MONITORING SYSTEM

Extraction System	Conditioning System	Analyzer System	Recorder/ Data Processor System
-Probe -Coarse/Fine Particulate Filter -Particulate/ Moisture Removal -Backpurge Connection -Calibration Gas Connection	-Transfer Line -SO_2 Scrubber* -TRS Oxidizer*	-Transfer Line -Fine Particulate Filter -Detection System -Calibration Gas System -Gas Mover -Flow Measurement Control Device	-Strip Chart Recorder -Data Logger

*If applicable

5.2 CONTINUOUS EMISSION MONITORING SYSTEM

5.2.1 TRS Extractive System Components

5.2.1.1 Particulate Filtration Device -

The main objective of the sampling probe is to extract a representative sample from the source and transport that sample to other components of the sampling train. The probe should be of such construction to minimize interaction between itself and the gas stream. If needed, the probe may require additional equipment to aid in particulate removal and moisture control application.

For particulate control, many designs have been used. They involve both in-stack and out-of-stack application.

The in-stack filters are divided into two categories: external or internal application.

The in-stack internal filter, as illustrated in Figure 5.3, normally consists of a porous cylinder made of various materials, such as: sintered 316 stainless steel, glass, ceramic or quartz. With this application, a baffle plate is usually incorporated with the filter to help deflect larger particulates from entering the porous filter.

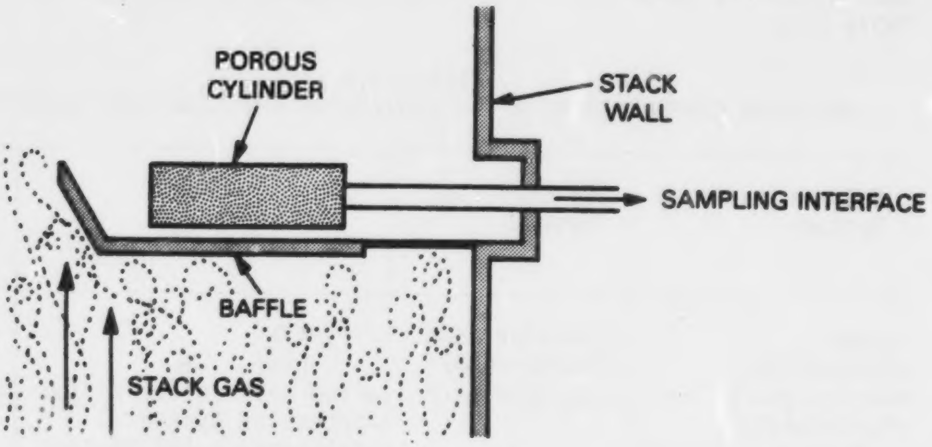
POROUS CYLINDER
STACK WALL
SAMPLING INTERFACE
BAFFLE
STACK GAS

Figure 5.3. In-Stack Internal Filter Configuration

Used under this application, a routine back-purge would normally assist in keeping the thimble clear of particulate.

Figure 5.4 illustrates the in-stack external filter arrangement. This configuration allows the adaption of a nozzle to the probe, pointing downstream of the gas flow, for gas extraction.

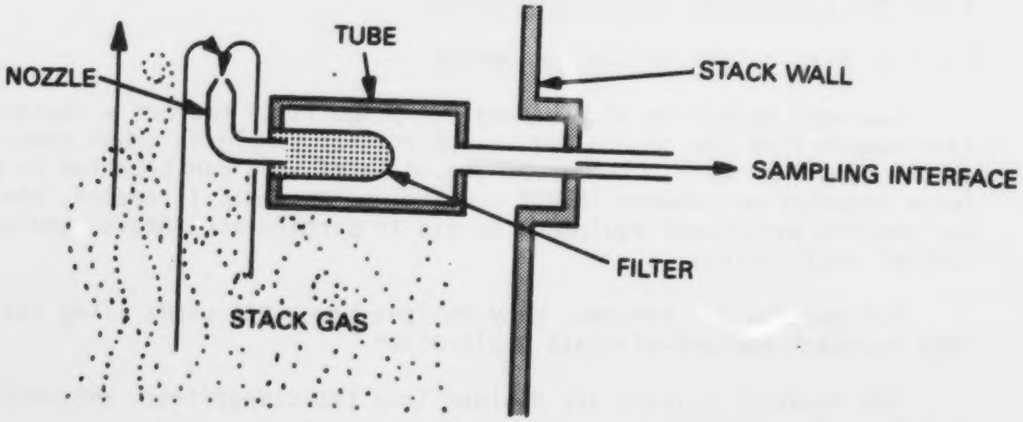
TUBE
NOZZLE
STACK WALL
SAMPLING INTERFACE
FILTER
STACK GAS

Figure 5.4. In-Stack External Filter Configuration

Since many of the recovery boilers and lime kilns contain a very large percentage of water, it is very important to keep the filter device above the water dew point. If not kept above the water dew point, the filter can become plugged with concentrate, causing a greater pressure drop across the system and loss of sample.

Filter plugging is the most common problem associated with gas extraction systems. To help eliminate the filter plugging problem, techniques such as backpurging periodically with air or steam have routinely been incorporated into a TRS CEM system. Other techniques such as Baffle plates and sheaths around the porous filter have also been utilized. These techniques are illustrated in Figure 5.5 and 5.6 respectively.

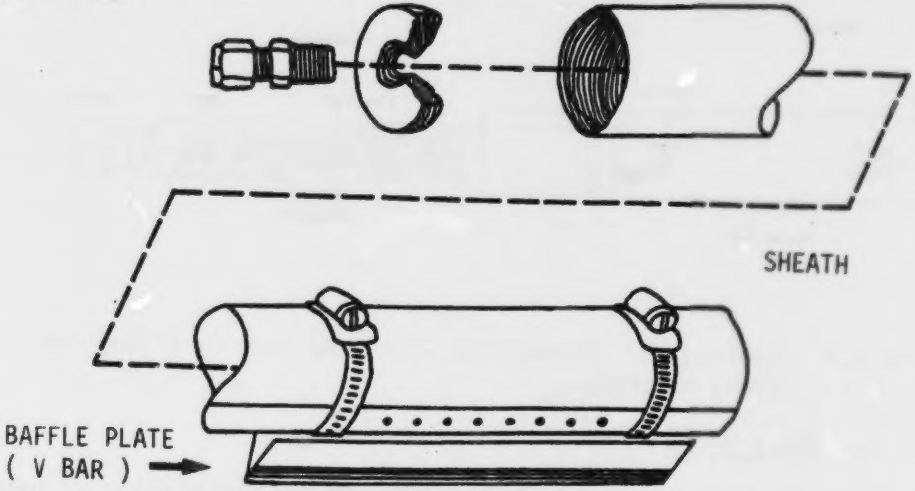

Figure 5.5. Use Of A Baffle Plate (V-Bar) And Sheath On A Lime Kiln Application.

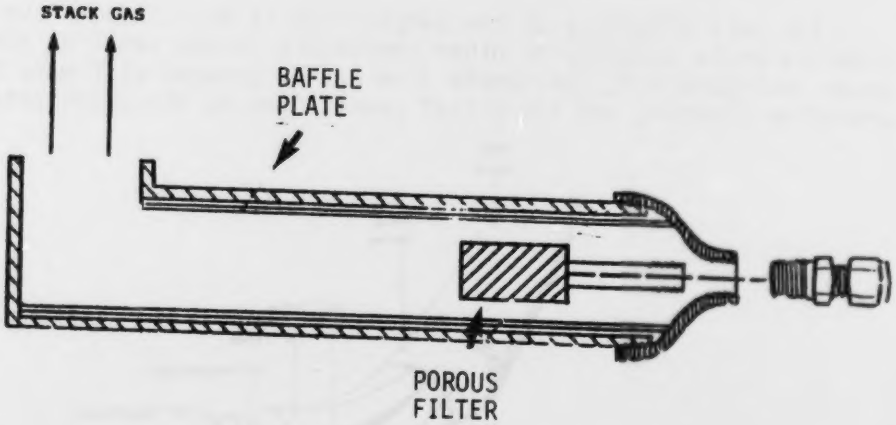

Figure 5.6. Recovery Furnace TRS Sampling Probe Utilizing A Porous Filter and a Baffle Plate.

Recently, the inertial filter has been used as a secondary filtering device in conjunction with a primary porous filter. In application, inertial filter extracts a gas sample from the main gas stream at a 90° angle. Within the probe, the high speed sample passes through a tubular (inertial) filter. A small portion of this sample is drawn radially through the porous filter wall at a velocity so low that the inertia of solid and liquid particulates will be too high to curve through the wall of the filter. Figure 5.7 illustrates the use of an inertial filter as part of the sampling probe assembly.

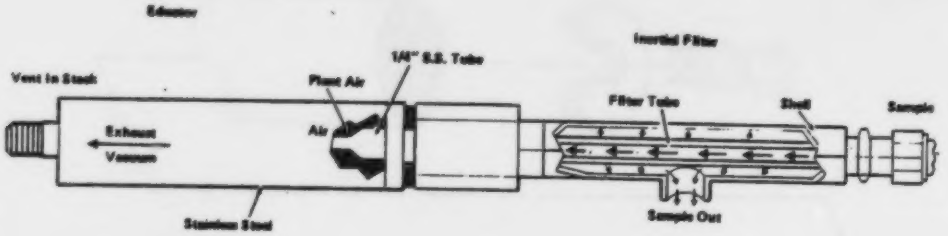
Eductor
Inertial Filter
1/4" S.S. Tube
Vent in Stack
Plant Air
Filter Tube
Shell
Sample
Air
Exhaust
Vacuum
Stainless Steel
Sample Out

Figure 5.7. Application Of Inertial Filter As Part Of A Sampling Probe Assembly.

5.2.1.2. Stack Probe

The sampling probe normally consists of two components: an outer sheath made of stainless steel and an inner lining made of either glass or teflon.

5.2.1.3. Sample Line

The main objective of the sample line is to transport the sample gas from the probe assembly to other components in the sampling train. As shown in Figure 5.8, the sample line may be grouped with many tubes providing plumbing and electrical connections to the probe assembly.

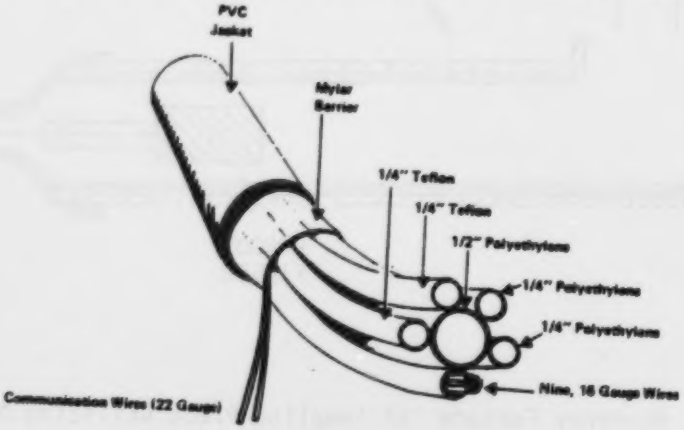
PVC Jacket
Mylar Barrier
1/4" Teflon
1/4" Teflon
1/2" Polyethylene
1/4" Polyethylene
1/4" Polyethylene
Nine, 16 Gauge Wires
Communication Wires (22 Gauge)

Figure 5.8. Umbilical Assembly

In this configuration, the sample line is part of a total bundle called the umbilical assembly.

Sampling train configuration will normally dictate important considerations when selecting sampling lines. Such considerations should include:

- Materials of construction;
- Size and length of sample line;
- Heat trace capability; and
- Cost.

5.2.1.3.1. Materials of Construction -

The choice of proper material of construction is very important. Acceptable material of construction must meet these important criteria:

- Material must have sufficient chemical resistance to withstand the corrosive constituents of the sample;
- Material must not exhibit excessive interaction (reaction, absorption, adsorption) with the sample gases;
- Material used near the stack must be heat resistant; and
- Material must be heated if moisture is not removed prior to sample transfer.

The corrosive constituently encountered in monitoring emissions from Kraft pulp mills involves many species. In particular, acid gases containing sulfuric and nitric gases are typical emissions. The chemical resistance of various materials to these constituents is summarized in Table 5.3.

TABLE 5.3

CHEMICAL RESISTANCE OF VARIOUS MATERIALS

Material	Dry SO_2	Dry NO_x	Dil. HNO_3	Dil. H_2SO_3	Dil. H_2SO_4	Conc. HNO_3	Conc. H_2SO_4
304 Stainless Steel	S (some pitting observed)	S	S	Q	U	S	U
316 Stainless Steel	S	S	S (<.051)*	S	S-Q (<.508)	S (<.508)	U (>1.27)
Carpenter 20 SS	S	S	S	S	S-Q	S	S
Aluminum	S	-	S (.127-.508)	S (.127-.508)	Q (.508-1.27)	U (>1.27)	U (>1.27)
Glass	S	S	S (<.127)	-	S (<.127)	S (<.127)	S (>.127)
Teflon	S	S	S	S	S	S	S
PVC	S	S	S	S	S - Q	U	S-Q
Tygon	S	S	S - Q	S	S	Q-U	S-Q
Polyethylene	S	S	S - Q	S	S	U	Q-U
Polypropylene	S	S	S	S	S	U	Q-U
Nylon		S	S	U	U	U	U
Viton	S - U	S	S	S	S	S-U	S-Q

*Quantities in parentheses indicate corrosion rates in mm per year.

S = Satisfactory
Q = Questionable
U = Unsatisfactory

5.2.1.3.2 Heat Resistance

Table 5.4 presents the heat resistance of various plastic materials. Depending upon the condition and extraction location, all materials are candidates for transfer material. The less heat resistant plastics (polypropylene and polyethylene) cannot be used as efficiently in close proximity to combustion sources. Teflon exhibits the best potential as a sampling line component between the probe and the rest of the system.

TABLE 5.4
MAXIMUM CONTINUOUS OPERATING
TEMPERATURES FOR PLASTICS

Material	Maximum Temp. (°C)
Teflon	250
Vivton	150
Polyethylene*	80-125.6
Polypropylene	110
Nylon	121.1
CPVC	110
Tygon*	60-82.2

*Depends on type used.

5.2.1.3.3. Sample Interaction

It is essential that the gas sample be transported from the probe to the rest of the system with minimum loss and interaction. There are several mechanisms by which interaction between sample gas and probe can occur. They are:

- reaction
- absorption
- adsorption
- dilution

Gas phase reaction in sampling lines can occur by homogeneous gas phase reaction and by heterogenous catalytic reaction. Materials of construction such as Teflon®, stainless steel or glass, are generally very poor catalyst and would not be expected to cause reactions. Absorption and adsorption by the walls of the transfer line would eventually reach equilibrium; consequently, would not change the concentration of the constituent stream. Studies have indicated that absorption and adsorption are negligible, in association to reduce sulfur compounds, for stainless steel, Teflon®, polypropylene, polyethylene and Tygon®.

5.2.1.3.4. Size and Length of Sample Line

The size of the sample line must be such that it is large enough so a pump can handle the pressure drop, yet small enough so the response time is not excessive. Flow rates as a function of pressure drop are shown for various line sizes in Figure 5.9.

Studies have shown that for a flow rate of two liters per minute, 6.35 mm I.D. tubing will give only a pressure drop of between 1 and 3 mm Hg per 100 ft. of tubing. This is not an excessive pressure drop for a sampling system.

The lag time , (t), for a sample line volume, (V), may be calculated as:

$$t = \frac{V}{F}$$

where:
t = Lag time, (sec), V = Sample line volume, (ft^3), F = Flow rate, (ft^3/sec).

As an example, for a tube with an I.D. of 6.35 mm and 100 ft. from sample extraction to the analyzer, what is the lag time at a flow rate of 2 l/min?

- 1st - Diameter of tube from mm to ft.
  $(6.35 \text{ mm})(32.808 \times 10^{-4} \text{ ft/mm}) = 0.0208 \text{ ft.}$
- 2nd - Calculate area of tube
  $A = \pi r^2 = \pi\left(\frac{D}{2}\right)^2 = \frac{\pi D^2}{4} = \frac{(0.0208 \text{ ft})^2}{4} = .0003398 \text{ ft.}^2$
- 3rd - Calculate volume of sampling line
  $V = (A)(L) = (0.0003398 \text{ ft}^2)(100 \text{ ft}) = 0.03398 \text{ ft}^3$
- 4th - Convert flow rate from l/min to ft^3/sec.
  $(2 \text{ l/min})(5.886 \times 10^{-4}) = .00117 \text{ ft}^3/\text{sec}$
- 5th - Calculate lag time using volume and flow rate
  $t = \frac{V}{F} = \frac{(0.03398 \text{ ft}^3)}{(0.00117 \text{ ft}^3/\text{sec})} = 29.0 \text{ sec.}$

For the above example, the lag time calculation would be 29 seconds. This lag time is well within EPA guidelines. Table 5.5 displays lag times for 100 feet of sample line with various inside diameters sample lines for flow rates of 1 and 2 standard liters per minute.

TABLE 5.5
SAMPLING LINE LAG TIME

Tubing Size (mm)	Lag Time per (30.48 m) length 1 liter per min	 2 liter per min
1.651 (3.175 o.d. x .762 wall)	3.58 sec	1.79 sec
3.175 (3.175 i.d.)	13.26 sec	6.63 sec
4.318 (6.35 o.d. x 1.016 wall)	24.54 sec	12.27 sec
4.572 (6.35 o.d. x 0.889 wall)	27.51 sec	13.75 sec
4.826 (6.35 o.d. x .762 wall)	30.64 sec	15.32 sec
6.35 (6.35 i.d.)	53.06 sec	26.53 sec
7.747 (9.525 o.d. x .889 wall)	1.32 min	0.658 min
9.525 (9.525 i.d.)	2.00 min	0.995 min
10.92 (12.70 o.d. x .889 wall)	2.62 min	1.31 min
12.70 (12.70 o.d.)	3.54 min	1.77 min

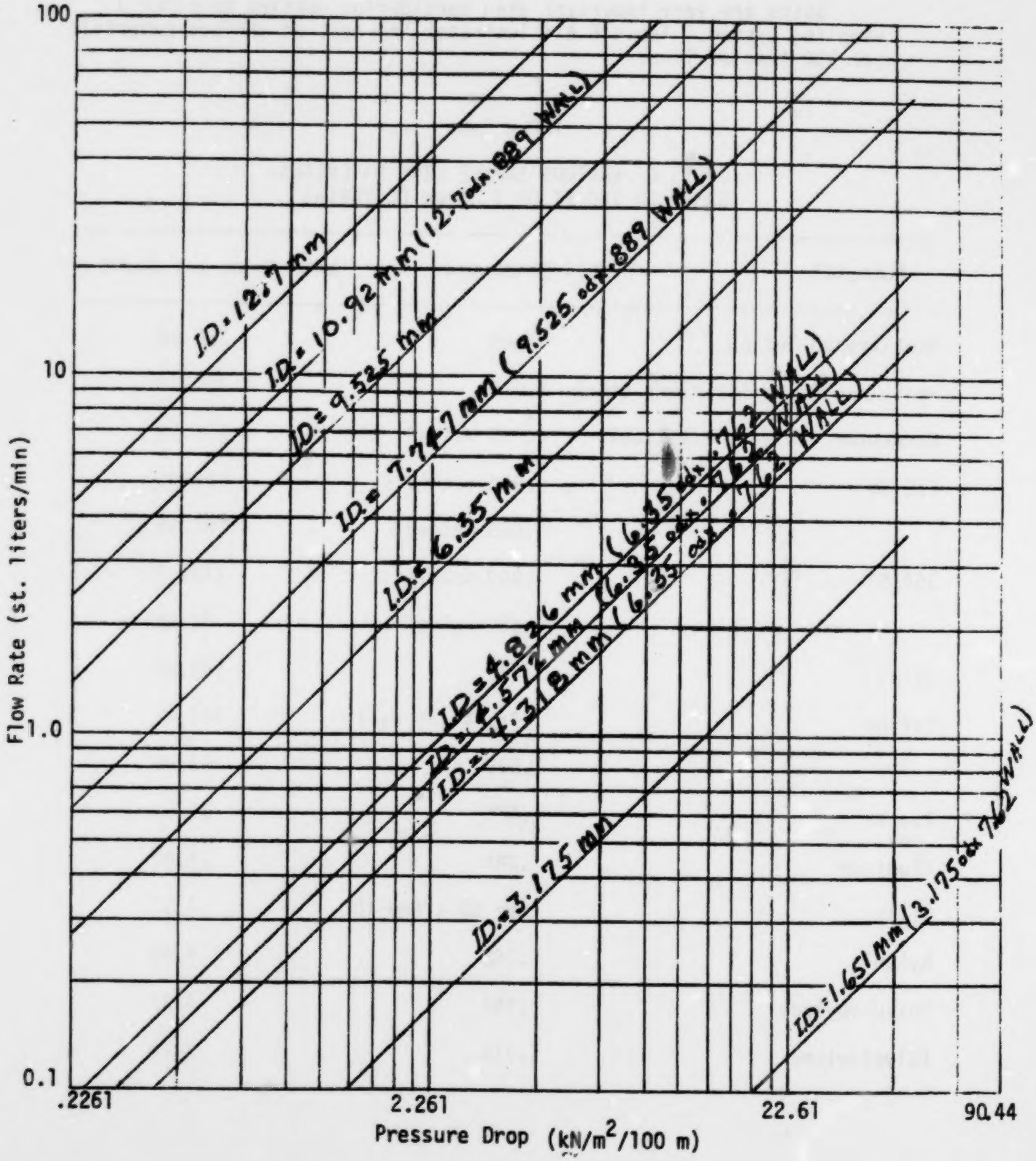

Figure 5.9. Flow Rates vs. Pressure Drop For Various Sample Lines Sizes

5.2.1.3.5. Cost -

Costs are very important when considering putting together a sampling system. Table 5.6 illustrates the cost of various materials per 100 feet of line.

TABLE 5.6

COSTS OF VARIOUS SAMPLE LINE MATERIALS
BASED ON 100 FT OF 6.35 mm OD TUBING

Material	Wall Thickness	List Price per 30.48 m
Heat Traced Teflon	.889	350.00
Heat Traced 316 Stainless Steel	1.016	325.00
Carpenter 20 Stainless Steel	.889 welded	196.00
316 SS	.889 seamless	184.45
	.889 welded	80.95
304 SS	.889 seamless	113.07
	.889 welded	71.66
Viton	1.575	145.00
Teflon	.787 stiff wall	107.00
	1.575	63.00
Tygon	1.575	15.60
Aluminum	.889	11.00
Glass	8mm OD x 6mm ID	7.33
Nylon	.762	4.40
Polypropylene	.787	4.31
Polyethylene	1.016	3.70

5.2.2. Conditioning System

5.2.2.1. - Moisture Removal -

Gases sampled from lime kilns and recovery boilers at Kraft pulp mills usually contain significant quantities of water vapor which, when cooled to room temperature, will condense out. There are presently very few analyzers which are insensitive to water vapor. For those analyzers, the sample gas is maintained above the water dew point by utilizing heat trace lines, heated filters and pumps and heated analyzer enclosures.

For analyzers which cannot operate with a large quantity of water vapor present, it is important that before analysis, it be removed as an interference. This can be accomplished through several techniques. They are: (1) Condensation; (2) Dessicant Technique; (3) Permeation Dryers; and (4) Sample Dilution.

5.2.2.1.1. Condensation -

Condensers are the most common form of cooling gas streams to permit moisture removal. They are generally temperature regulated either by circulating fluid outside the condensing surfaces or by circulating air.

Figure 5.10 illustrates the use of an air cooled double vortex condenser in a TRS CEM system.

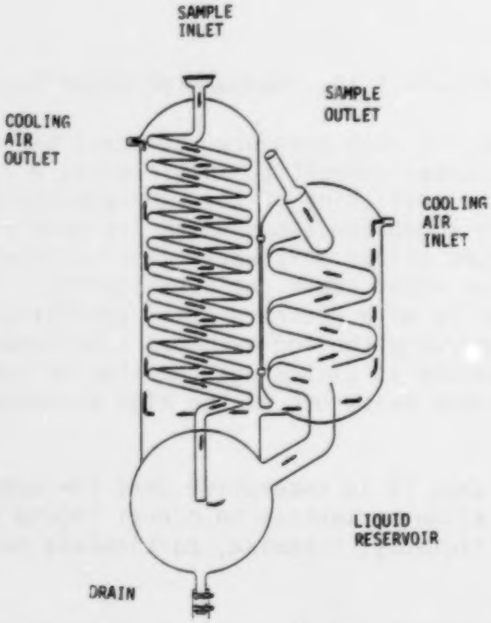

Figure 5.10. Use Of An Air Cooled Double Vortex Condenser In A TRS CEM System.

Because a liquid is condensed from the gas stream, an automatic drain valve should be incorporated into the system to eliminate gas absorption in the condensate.

5.2.2.1.2. Permeation Dryer -

In recent years the permeation dryer has become increasingly popular with extractive CEM systems. Utilizing a non-contact technique, the permeation dryer is composed of ion-exchange membrane fuses housed in a hollow stainless steel tube, as illustrated in Figure 5.11. This type of dryer is termed a tube-and-shell-type.

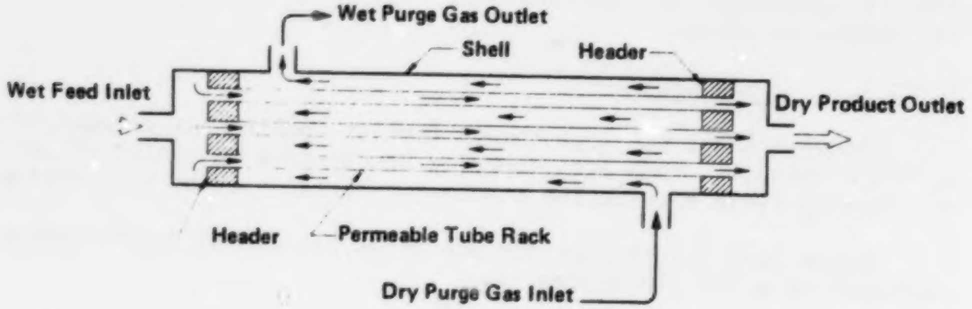

Figure 5.11. Permeation Dryer Technique

In operation, the high pressure wet stack gas enters the dryer through the tube side. Counter current to this flow is a low pressure dry purge gas supplied to the shell side of the tube-and-shell. This differential pressure is sensed along the tubes which are made of ion-exchange membrane. This unique membrane allows only water vapor molecules to permeate through its skin, retaining other stack gas constituents. The movement of water molecules is from the high pressure stack gas stream to the low pressure purge gas stream through the ion-exchange tube membranes. The now water-laden purge gas stream is exited out the side of the dryer. The water-free stack gas stream exits out of the high pressure outlet side of the condenser.

One can see that it is imperative that the entering water be above its dew point to allow permeation to occur: liquid water plugs the system, decreasing its efficiency; likewise, particulate decreases the operation of the dryer.

Some of the advantages for using a permeation dryer over a condenser are:

- non-contact technique - less acceptable to corrosion;
- less possibility of sample loss in condensate;
- no condensate trap required; and
- competitively priced.

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Some of the disadvantages are:

- o plugging of the ion-exchange membrane tubes due to particulate; and
- o required hardware associated with the low pressure dry purge gas inlet.

5.2.2.2. SO_2 Separation Devices -

For these systems that measure reduced sulfur compounds as SO_2, the stack gas SO_2 must be removed prior to sample analysis to prevent a positive bias. Early TRS CEM systems employed wet chemical scrubbers to remove the interfering SO_2 pollutant, while allowing the reduced sulfur compounds to pass. Recently, dry bed scrubbers have been employed equally well. Using either system, the user must be aware of potential drawbacks. They are:

- o Solubility/Reactivity with scrubber media by reduced sulfur compounds;
- o SO_2 breakthrough potential;
- o Maintenance/Upkeep of scrubber media;
- o Monitor response to scrubber deterioration;
- o Residence time; and
- o Variable SO_2 concentrations.

5.2.2.2.1. Wet SO_2 Scrubbers -

A wet SO_2 scrubber is selected on the basis of SO_2 solubility in the scrubber (buffer) solution. A buffered solution of potassium citrate (pH 5.5-5.6) has been found to be optimum for retarding SO_2 while allowing reduced sulfur compounds to pass through. The scrubber system can either be "batch" or "continuous" removal technique.

A batch scrubber is normally a solution of potassium citrate-citric acid in a series of glass or Teflon® impingers. In operation, the gas is pulled through the impingers, allowing the SO_2 to be absorbed while passing the reduced sulfur compounds. Periodically, the scrubber solution is changed as it becomes "exhausted."

Continuous SO_2 scrubber systems are different from batch scrubber systems in the fact that a fresh buffer solution is constantly fed into the container while the expended solution is removed. Continuous SO_2 scrubbers require more maintenance, but better response time is provided than with the batch scrubber.

Figure 5.12 illustrates the "batch" SO_2 scrubber while Figure 5.13 illustrates the two-stage "continuous" SO_2 scrubber.

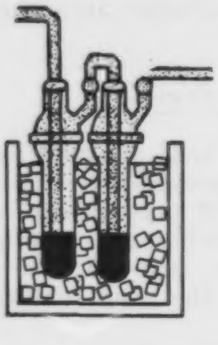

Figure 5.12. "Batch" SO_2 Scrubber

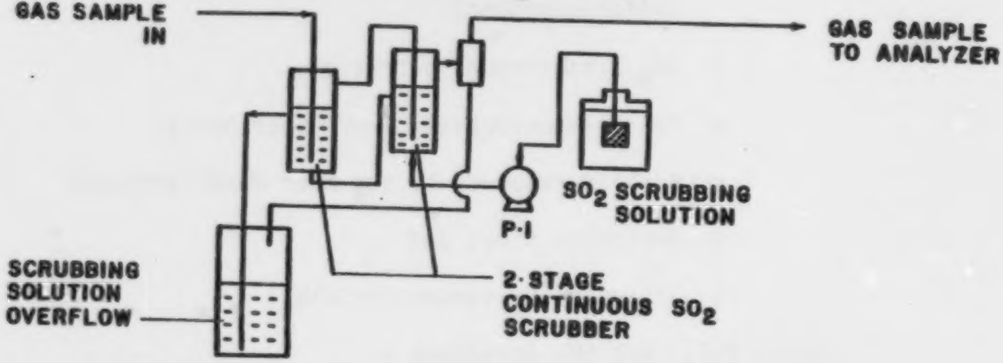
GAS SAMPLE IN
GAS SAMPLE TO ANALYZER
SO_2 SCRUBBING SOLUTION
P-1
SCRUBBING SOLUTION OVERFLOW
2-STAGE CONTINUOUS SO_2 SCRUBBER

Figure 5.13. "Continuous" SO_2 Scrubber

5.2.2.2.2. Dry Bed Scrubber -

In recent years, dry bed scrubbers for SO_2 removal have been replacing wet scrubbers. Dry bed scrubbers normally employ resin beads impregnated with a solution which has a high absorbability for SO_2 while rejecting reduced sulfur compounds. The gas sample is once again pulled through the cartridge, allowing the gas stream to contact the impregnated resin beads. The SO_2 is retained on the beads while the reduced sulfur compounds pass unaffected. The dry bed scrubber requires less maintenance than the wet scrubber. However, breakthrough is possible after exhausting all active sites on the resin.

5.2.2.3. TRS Oxidizer -

For those detection principles which detect the presence of sulfur dioxide (SO_2) rather than total reduced sulfur (TRS), the stack gas TRS components must be oxidized to SO_2. Studies have indicated the best available and most cost effective technique is a heated quartz tube, as illustrated in Figure 5.14.

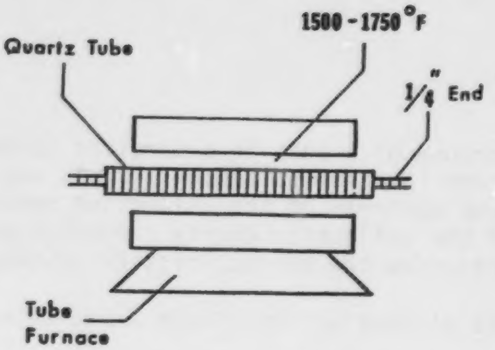

Figure 5.14. Heated Quartz Tube TRS Oxidizer

The main objective of the oxidation furnace is to oxidize the major reduced sulfur compounds to SO_2. However, it is desirable not to oxidize carbonyl sulfide (COS) or SO_2 to SO_3. This would, in effect, bias all measured results.

Three important factors which govern what is oxidized in the furnace are:

- Oxygen concentration in the sample;
- Furnace temperature; and
- Sample residence time in the furnace.

5.2.2.3.1. Oxygen Concentration in Gas Sample -

Because of the nature of the process at Kraft pulp mills, it is believed that a sufficient amount of sample oxygen (∿ 5%) is available to allow complete combustion of major reduced sulfur compounds in the sample gas. However, it is advisable to verify this periodically by injecting a known concentration of certified H_2S gas at the inlet of the probe along with the stack gas sample. If the monitor responds properly (± 5% of certified value), then the system is operating properly.

5.2.2.3.2 Furnace Time and Temperature -

Field experience has indicated that the furnace temperature should be maintained between 1500-1750°F for effective combustion of reduced sulfur compounds. Studies have indicated that maintaining this temperature insures 100% conversion efficiency for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, while only 25% of the carbonyl sulfide (COS) present is oxidized to SO_2. However, the presence of COS in recovery furnace flue gas has been found to be less than 5% of the total reduced sulfur compounds at a level of 10 ppm. This concentration would be fairly insignificant compared to the final TRS value. Temperatures greater than 2000°F are required to oxidize SO_2 to SO_3 without an active catalyst. Field experience has demonstrated a residence time of 2.5 to 5 seconds in the combustion tube is sufficient for oxidation.

In summary, a thermal oxidation furnace should be constructed of quartz tube heated to 1500-1750°F with a sample residence time of 2.5 to 5 seconds.

5.2.2.4 Pumps -

The main purpose of a pump in a sampling system is to transfer the gas stream from one location to another. This may be done either by positioning the pump upstream of the collection service (positive pressure) or downstream of the collection device (negative pressure). The pump location will determine the characteristics of that pump.

Pumps can be divided up into three broad categories:

(a) positive displacement pumps,
(b) centrifugal pumps, and
(c) eductor.

5.2.2.4.1 Positive Displacement Pumps -

Positive displacement pumps can be characterized by a linear relationship between the change in capacity (ΔQ) of the pump and the pressure drop (ΔP) across the pump. In essence, as the volumetric flow rate changes, there is a concurrent and direct change in pressure drop across the pump. This becomes a constant. Figure 5.15 represents this characteristic of the positive displacement pump.

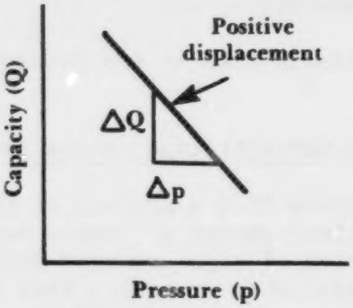

Figure 5.15. Positive Displacement Pump Characteristics

The name positive displacement pump arises from the fact that air is displaced by the movement of the inner components of the pump. The mechanism by which the moving part displaces the air determines the principle of operation. For example, pumps containing fixed casings with movable pistons are called reciprocating pumps, part of the positive displacement classification. Those pumps which utilize a gear or lobe to move air are called rotary pumps. Table 5.7 illustrates the two subdivisions of the positive displacement pumps.

TABLE 5.7
SUBDIVISIONS OF POSITIVE DISPLACEMENT PUMPS

Principle of Operation	**Type of Pump**
Reciprocating	piston plunger diaphragm
Rotary (not discussed in this manual)	gear lobe vane screw rotary plunger

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The piston pump is characterized by the movement of a piston into and outside of a fixed volume. The piston displaces the air occupying the same space on the discharge side. Likewise, the air displaces the piston on the suction side. Figure 5.16 demonstrates the action of the piston (reciprocating) pump.

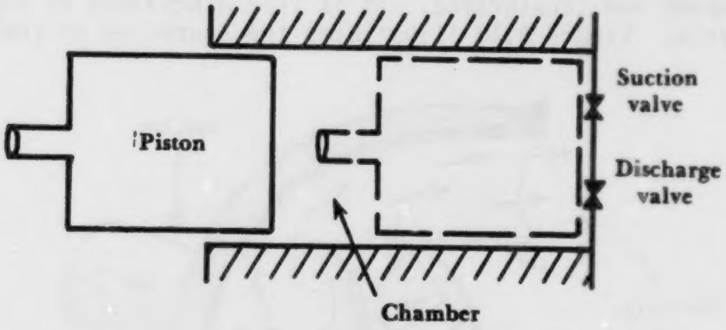

Figure 5.16. Reciprocation Pump

The reciprocating pump is by far the most common pump used in sampling trains. The operation is very similar to the piston pump. Once again, air is displaced by movement of a diaphragm, the outer edges of which are bolted to a flange on the pump casing. The diaphragm may be made of metal, Teflon®, or neospore. The most important characteristic of the diaphragm material is its flexibility and resistance to reaction with the air being moved. As the diaphragm moves up, air flows into the pump via a suction valve. As the diaphragm moves down, air is funneled through a discharge valve. Consequently, the gas moves into and out of the pump.
Figure 5.17 illustrates the operation of a typical diaphragm pump.

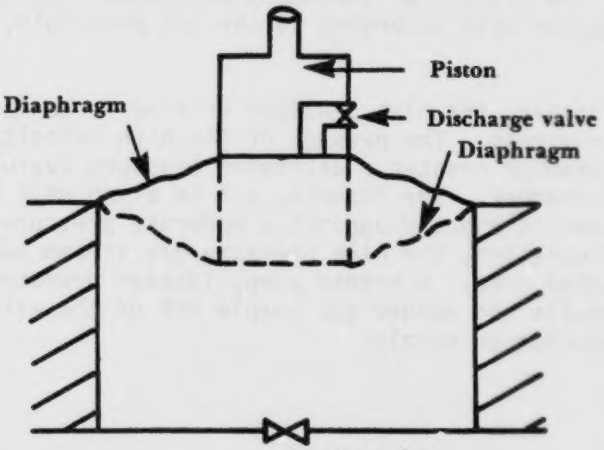

Figure 5.17. Diaphragm Pump

5.2.2.4.2. Centrifugal Pump -

Different from the positive displacement pumps, centrifugal pumps employ centrifugal force to move air. The movement of an impeller rotating in a volute ("snail's shell") casing causes a differential pressure, thus pulling air into the center of the shaft. The air is then picked up by the rotating vanes and accelerated. It is then discharged by way of the discharge nozzle. Figure 5.18 illustrates the operation of the centrifugal pump.

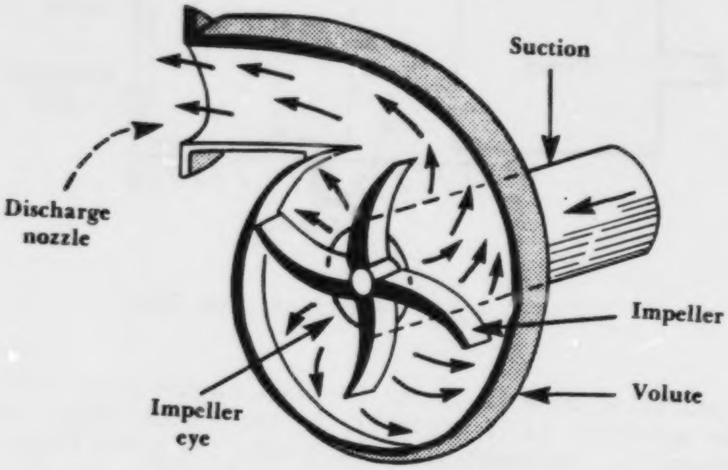

Figure 5.18. Centrifugal Pump

5.2.2.4.3 Air Driven Eductor -

Air driven eductors are becoming more prevalant as the pump in a TRS CEM sampling train configuration. Present application of the eductor has been both as the primary or secondary air mover. In the primary configuration, the eductor acts according to the jet principle, as depicted in Figure 5.19.

At the nozzle, the high pressure driving force is converted into a high velocity stream. The passage of the high velocity stream through the suction chamber creates a decreased pressure (vacuum), thus drawing air into the chamber. The incoming air is mixed with the high velocity gas mixture and is ejected against a moderate pressure through a diffuser. In this configuration, the high pressure gas stream pulls the stack gas into the eductor area. A second pump, located downstream of the conditioning system, pulls the needed gas sample off of the air inlet position before the eductor or nozzle.

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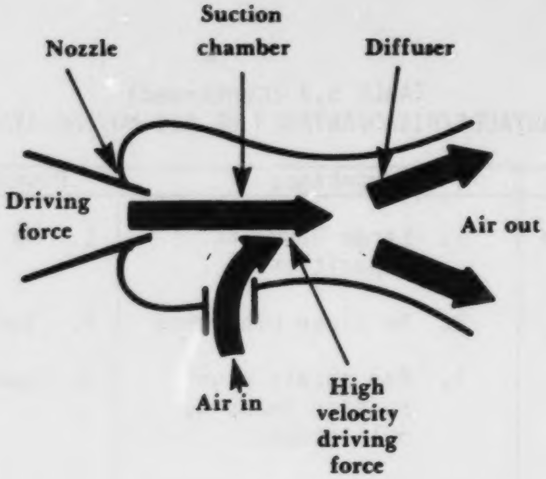

Figure 5.19. Air Driven Eductor

It is evident from the above discussion that there are many choices available in selecting a pump. A comparison of some of the advantages and disadvantages of certain pumps is given in Table 5.8.

TABLE 5.8
ADVANTAGES/DISADVANTAGES OF AIR MOVING SYSTEMS

Pump type	Advantages	Disadvantages
Piston pump (reciprocating)	1. Can operate at high suction pressure 2. Can be metered	1. Small capacity 2. Seal required between piston and piston chamber 3. Working parts such as check valves and piston rings may cause difficulties 4. Pulsating flow 5. Moderate maintenance
Diaphragm pump (reciprocating)	1. Wide range of capacities 2. No seal required 3. Good in continuous operation	1. Limited materials of construction 2. Operation at limited suction pressures 3. Pulsating flow 4. Periodic diaphragm replacement 5. Moderate maintenance

TABLE 5.8 (Continued)
ADVANTAGES/DISADVANTAGES OF AIR MOVING SYSTEMS

Pump type	Advantages	Disadvantages
Centrifugal pump	1. Large Range of capacities 2. No close clearance 3. Can obtain high suction heads by multistages 4. Light maintenance	1. No small capacities 2. Turbulence 3. Operational noise
Eductors	1. No moving parts 2. Limited hardware in contact with gas stream	1. Requires unrestricted flow 2. Plugging in exit port of eductor 3. May require steam to help dislodge particles

5.2.3 DETECTOR SYSTEM

As indicated earlier, many analytical techniques are available for monitoring TRS emissions from Kraft pulp mills. The techniques either employ some form of direct measurement of the TRS components (gas chromatographic) or remove SO_2 from the gas stream, then oxidize the remaining TRS to SO_2 with detection as SO_2. The following section discusses the most common detection principles utilized in continuous emission monitoring for TRS.

5.2.3.1 Electrochemical Transducers -

One of the most popular methods of detecting SO_2 in a gas stream is the electrochemical transducer. The electrochemical transducer consists of a sensing membrane, electrolytic reservoir and a counter electrode, all in a self-contained cell, as illustrated in Figure 5.20.

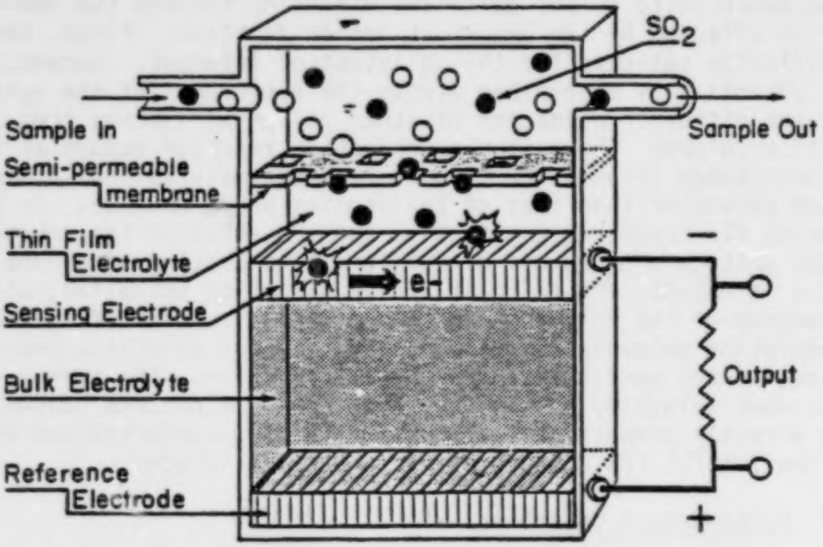

Figure 5.20. Electrochemical Transducer

The transducer is generally a self-contained electrochemical cell in which a chemical reaction takes place involving the pollutant molecule. Two basic techniques are used in the transducer: (a) the utilization of a selective semipermeable membrane that allows the pollutant molecule to diffuse to an electrolytic solution, and (b) the measurement of the current change produced at an electrode by the oxidation or reduction of the dissolved gas at the electrode.

In operation, the flue gas is drawn into the electrochemical transducer, where the selective semi-permeable membrane allows only the SO_2 pollutant gas to diffuse. The SO_2 undergoes electro-oxidation, releasing electrons. The net reaction is a release of electrons to the counter-electrode by means of the electrolyte reservoir, as illustrated in the following equation:

$$SO_2 + 2H_2O \longrightarrow SO_4^{-2} + 4H^+ + 2e-$$

If the flow of electrons is diffusion controlled, the current will be directly proportional to the concentration of reactants. This is known as Fick's Law of Diffusion. Mathematically, this can be stated by the following equation:

$$i = \frac{nFADc}{\delta} = kc$$

where: i = current in amps;
n = number of exchanged electrons per mole of pollutant;
F = Faraday constant (96,500 coulombs);
D = diffusion coefficient of the gas in the membrane and film;
c = concentration of the gas dissolved in the electrolyte layer (moles/μm^3);
A = thickness of the diffusion layer, in cm.

The selectivity of one pollutant diffusing through the membrane over another is affected by two important design features. First, the membrane is specifically selected for the pollutant of interest. Second, a retarding potential is maintained across the electrodes of the system to prevent the diffusion/oxidation of other pollutant species that are not as easily oxidized. The oxidation-reduction reaction occurs at the sensing electrode because the counterelectrode material has a higher oxidation potential than that of the species being reacted. In the cell, the sensing electrode has a potential equal to that of the counterelectrode minus the voltage drop across a register. The sensing electrode is electrocatalytic in nature, and being at a high oxidation potential, will cause the oxidation of the pollutant and a consequent release of electrons. Other pollutant molecules, having higher or lower oxidizing potential, therefore, cannot participate in the cell reaction. The system therefore, becomes selective by design. The flow of electrons consequently becomes directly proportional to the initial SO_2 concentration which reflects the initial TRS concentration in the gas stream.

5.2.3.2 Fluorescence Detection -

Another popular technique for monitoring SO_2 in a gas stream is fluorescence spectroscopy. Fluorescence spectroscopy is a photoluminescent process in which the SO_2 molecule absorbs light of a given wavelength and re-emits this light at a different wavelength. This release of energy is directly proportional to the original concentration of SO_2 present. As illustrated in Figure 5.21, the conditioned gas sample is brought into the measurement chamber for excitation.

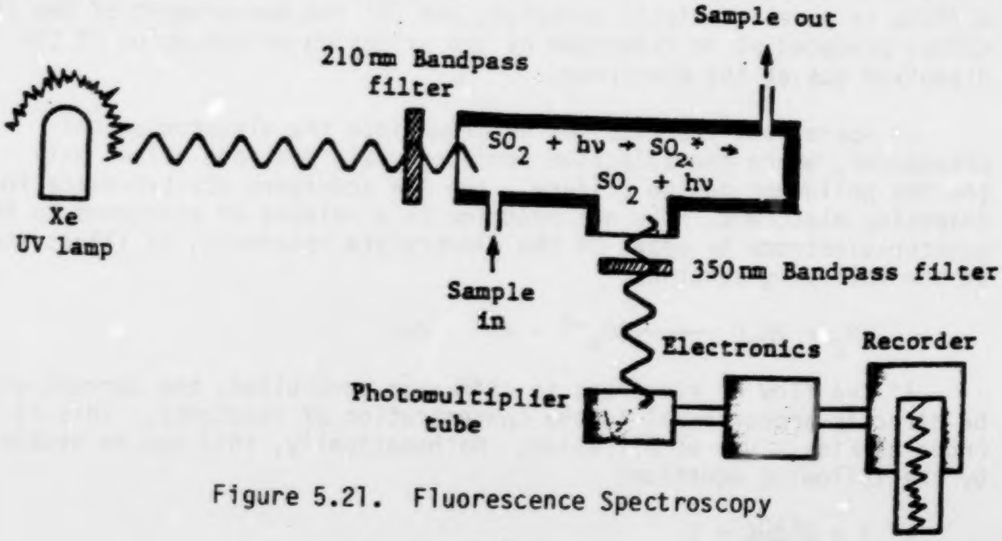

Figure 5.21. Fluorescence Spectroscopy

An ultraviolet (UV) lamp provides the needed energy to excite the SO_2 molecule to a higher energy state. The UV energy ($h\nu$) can be a constant or pulsed source. As the SO_2 molecule absorbs this energy, it becomes an electronically excited molecule, as illustrated in the following equation:

$$\underset{\text{ground state}}{SO_2} + h\nu \longrightarrow \underset{\text{excited state}}{SO_2^*} \quad \text{Absorption}$$

In this process the excited molecule will remain excited for about 10^{-4} to 10^{-3} seconds. During this period of time, the molecule will dissipate some of this energy in the form of vibrational and rotational motion. However, most of the energy will be re-emitted as light energy ($h\nu$) at a longer wavelength. Figure 5.22 demonstrates the difference between the absorption and fluorescence spectrum for the SO_2 molecule.

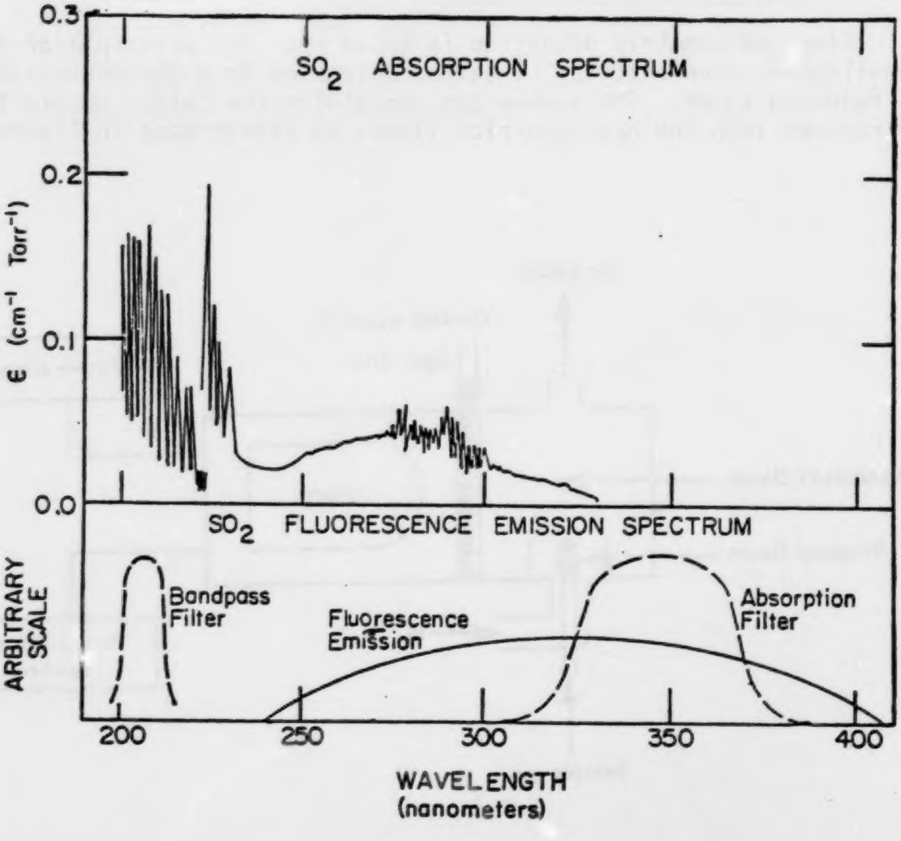

Figure 5.22. Absorption/Fluorescence Spectrum for the SO_2 Molecule

The re-emittance of light can be illustrated in the following equation:

$$\underset{\text{excited state}}{SO_2\,*} \longrightarrow \underset{\text{ground state}}{SO_2} + h\nu \qquad \text{Fluorescent}$$

A photomultiplier tube is used to change the emitted light energy into an electronic signal. A bandpass filter in front of the photomultiplier tube allows only the energy of interest to strike the tube.

Because of interference from water and hydrocarbons, those pollutants must be removed before sample analysis. In addition, calibration of the instrument must be performed with SO_2 in nitrogen or SO_2 in air, but not interchangeably. If one calibrates the instrument in SO_2 in nitrogen, then the source should have the same level of nitrogen as the span gases. Fluorescence detection, outside of this quenching problem, has no other significant interference problems.

5.2.3.3 Flame Photometric Detection -

Flame photometric detection is based upon the principle of a chemiluminescence reaction of sulfur molecules in a hydrogen-rich or reducing flame. The sample gas containing the sulfur specie is introduced into the hydrogen-rich flame, as illustrated in Figure 5.23.

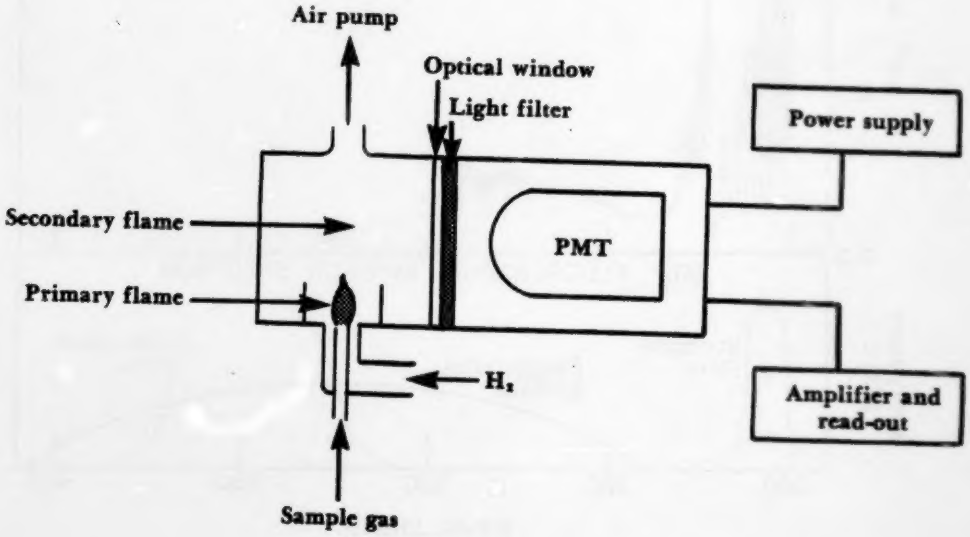

Figure 5.23. Flame Photometric Spectroscopy

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Within the primary flame, the sulfur reacts to provide a S_2 species. As the S_2 specie migrates from the primary flame to the outer cooler gases, an excited S_2* molecule is formed by the following equation:

$$\cdot H + \cdot H + S_2 \rightarrow H_2 + S_2^*$$

or

$$\cdot H + \cdot OH + S_2 \rightarrow S_2^* + H_2O$$

This sulfur specie (S_2^*) is in a very excited state. Consequently, it remains in that state momentarily, then converts to a lower energy state. It is this transformation from a high energy state to a lower energy state that the molecule releases energy as a strong luminescent emission ($h\nu$), as illustrated in the following equation:

$$S_2^* \rightarrow S_2 - h\nu$$

The observed luminescent emission ($h\nu$) is monitored by a photomultiplier tube and is directly related to the concentration of the sulfur pollutant present by the following equation:

$$I_{S_2} = I_o[S]^n$$

Where:

I_{S_2} = observed intensity of the molecular emission due to the S_2 species

$[S]$ = concentration of sulfur atoms

I_o = constant under given experimental conditions

n = constant (usually assumed to be 2) under given experimental conditions

The original concentration of sulfur molecules present in the gas stream becomes directly proportional to the amount of light emitted. Due to the non-linearity of observed light intensity to the concentration of sulfur pollutant present, most instruments use a linearizing electronic circuitry to yield a linear output voltage.

Since all sulfur species burn in the flame differently, it is imperative that the instrument be calibrated with a particular pollutant gas of interest. Likewise, since the detection principle cannot distinguish between different sulfur compounds, added instrumentation must be used to selectively remove unwanted sulfur species. This can be accomplished by dry bed scrubbers, liquid scrubbers or gas chromatography techniques.

5.2.3.4 Coulometric Detection -

Coulometric detection of SO_2 in a gas stream has been widely used in ambient monitoring. The technique utilizes the electrical charge generated by either the oxidation or reduction of a pollutant gas in the electrolytic cell as a direct correlation to measuring pollutant gas concentration. One of the common configurations of this detection principle consists of four electrodes in a reactor cell as illustrated in Figure 5.24.

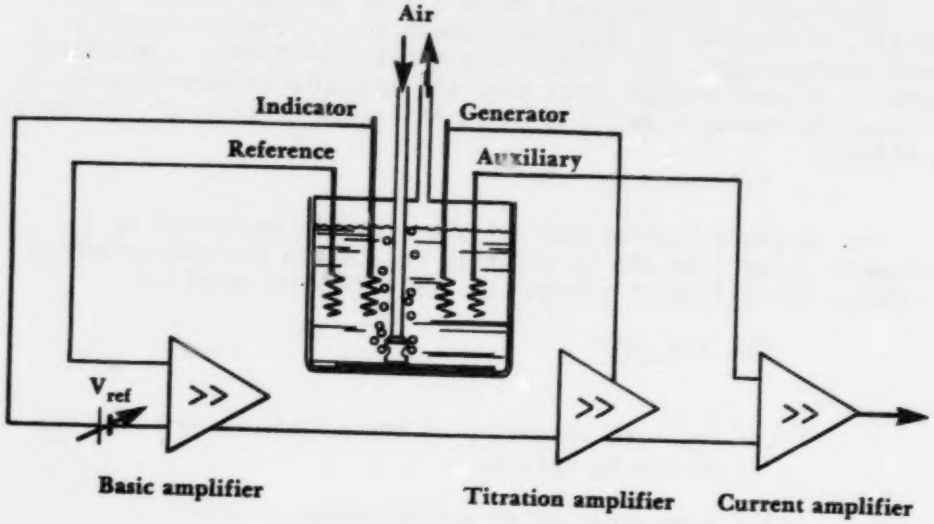

Figure 5.24. Coulometric Technique

It is within this "titration" cell that the SO_2 in the gas stream reacts with the bromine to produce a flow of electrons.

Typically, bromine concentration is maintained at a constant level by a set of indicator-reference electrodes and the electronic circuits. As sulfur dioxide is introduced into the detector cells, the bromine (Br_2) concentration is reduced by the reaction.

$$SO_2 + Br_2 + 2H_2O \rightarrow 2H_2SO_4 + 2\,Br^- + 2H^+$$

This reaction disturbs the Br_2/Br^- ratio, and this change is sensed by a basic amplifier. The current required to regenerate the bromine (Br_2) through the generator-auxiliary electrodes is proportional to the sulfur dioxide concentration. The gas sample passes continually through the titration cell at a constant flow rate. When there is no SO_2 in the gas stream, a constant level of bromine is maintained in the cell by the platinum wire generating electrode located at the end of the gas cell inlet. If SO_2 is present in the gas stream, then the constant concentration of bromine in the "titration" cell is interrupted. This causes the sensing electrode to vary the current supplied to the platinum wire, thus generating more bromine to bring the system back into equilibrium.

At the anode, the following reaction occurs:

$$2Br - 2e^- \rightarrow Br_2$$

and at the cathode, the reverse reaction occurs:

$$Br_2 + 2e^- \rightarrow 2Br$$

When excess bromine is generated, a depolarization current flows and is proportional to the bromine concentration. The concentration can be determined by Faraday's Law, which states that one gram equivalent of a material is oxidized or reduced by one Faraday of electricity. By measuring the current across the cell, the concentration of the sample may be determined since the quantity of electricity (Q, coulombs) is given as the integral of current (i, amperes) over the time interval (t, seconds):

$$\int_0^t (i)dt = Q = \frac{zmF}{M}$$

Where: m = mass in grams of the species consumed or produced during electrolysis

M = gram molecular weight

z = number of Faradays (equivalents) of electricity required per gram mole (i.e., the number of electrons appearing in the equation for the net reaction of interest)

F = proportionality constant: 96,487 coulombs/mole

This type of coulometric technique measures the amount (i.e., coulombs) of electricity directly produced as the result of a reaction of a pollutant at the electrode.

In current instrumentation, however, pollutant concentration is determined indirectly by measuring the current required to maintain a constant bromine (Br_2) concentration. The sample gas passes through an electrolysis cell and oxidizes the halogen to halide (for example, Br_2 + pollutant $\rightarrow Br^-$), thereby reducing the halogen concentration. The current required to maintain the electrochemical balance is directly proportional to the pollutant concentration.

5.2.3.5 Gas Chromatography Detection -

Gas chromatography is a process by which a mixture is separated into its constituents by a moving phase passing over a sorbent. The technique is similar to the widely practiced liquid-liquid partition column chromatography except that the mobile liquid phase is replaced by a moving gas phase.

The basis of the method lies within the separation column. In gas solid chromatography, this consists of a solid, porous absorbent packed in a small thin tube. The packed column is normally 4 mm (i.d.) tubing of stainless steel, copper, or glass, either bent into a u-shape or coiled. Lengths vary anywhere from 120 mm to 150 mm. It is the ability of the column to separate a gas stream into its constituents which enables the GC to efficiently operate as a TRS monitor.

Basically, gas chromatography consists of five basic parts: (1) pressure regulator and flow meter for carrier gas; (2) sample injection system; (3) separation column; (4) detector, and (5) strip chart recorder, as displayed in Figure 5.25.

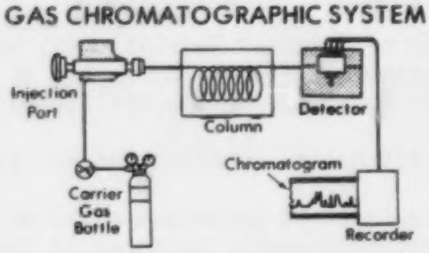

Figure 5.25. Typical GC System

5.2.3.5.1. Carrier Gas -

A high pressure gas cylinder serves as the source of the carrier gas. Commonly used gases are hydrogen, helium and nitrogen. The carrier gas should be:

- o inert to avoid interaction with the sample or solvent,
- o able to minimize gaseous diffusion,
- o readily available and pure,
- o inexpensive, and
- o suitable for detector use.

The basic function of the carrier gas is to transport the sample from the injection port through the column to the detector without interfering with the analytical technique.

5.2.3.5.2. Injection Port -

The injection port must be able to allow the introduction of the sample into the system without fractionation, condensation or adsorption in other components of the system. Typically, injection ports are heated to insure that the integrity of the sample does not change.

Historically, gas samples were injected into the GC through a self-sealing silicon rubber septum by a gas-tight syringe. Technique has to be quite good in order to inject the same amount of gas into the system each time. Consequently, gas-sampling valves were introduced to insure precision injections. In their simplest forms, they include a system of stopcocks or valves operated by compressed air. Between the valves is a sample loop of known volume. Gas from this sample loop is introduced into the GC by rotating a valve to connect the loop with the carrier gas.

5.2.3.5.3 Chromatographic Column -

Once the gas is introduced into the carrier gas stream, it is moved to the chromatographic column where separation occurs. As illustrated in Figure 5.17, the column is composed of a liquid phase on a solid adsorbent packed in a tube. The selection of the liquid depends upon the pollutant to be separated. For sulfur compounds, the recommended column is Teflon tubing packed with 30/60 mesh Teflon coated with 10% Triton X-305 solution.

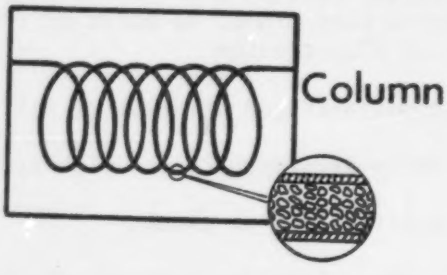

Figure 5.26. Chromatographic Column

As the sample gas passes through the column, different species of sulfur compounds will be retained on the column.

The retention of the pollutant on the column depends upon its interaction with the solid support and liquid phase of the packing. As the carrier gas moves the pollutant through the column, the more easily adsorbed sulfur compounds will be retained first while others flush through. This separation depends upon:

- solvent properties of the liquid support,
- column temperature,
- solute-solvent interaction, and
- other factors.

As the separated pollutants exit the column, they are sensed by the detector, as illustrated in Figure 5.27, and recorded by a data processor.

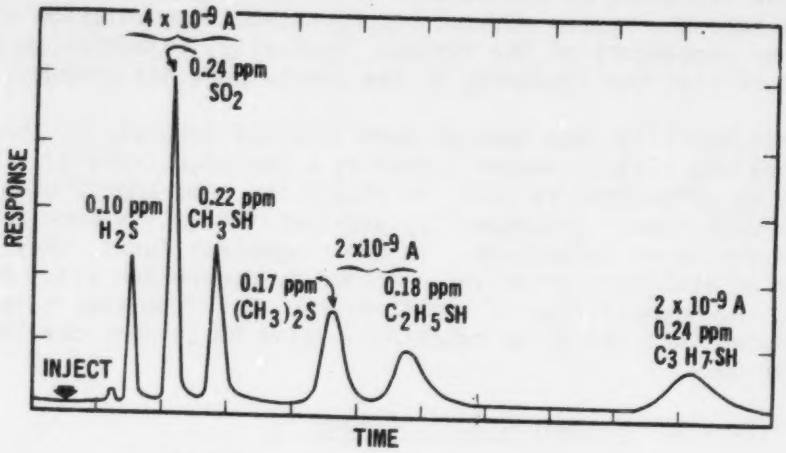

Figure 5.27. GC Chromatogram

5.2.4 Data Handling System

The data handling system is the last component of the TRS continuous emission monitoring system. Data handling systems can perform many tasks. Basically, the system receives the input signal from the TRS and diluent monitor and converts that signal to units of the standard. The data handling system can also provide

- instantaneous/averaged printout of pollutant concentration,
- perform daily zero/span checks with appropriate adjustments,
- perform quality control check,
- signal warning/alert for high or out-of-control situations, and
- provide maintenance and input notation.

All of the above functions are important tools in a source quality assurance program.

The most important functions of the data handling system are

- emissions corrected to a percent oxygen, and
- moisture correction.

5.2.4.1 Emissions Corrected to A Percent Oxygen -

Subpart BB specifies that the TRS concentrations for a 12-hour average must be corrected to 10 percent oxygen for lime kilns incinerators or other devices and 8 percent oxygen for recovery furnaces. This can be expressed by the following equation:

$$C_{corr} = C_{meas} \left[\frac{21 - X}{21 - Y} \right]$$

where:

C_{corr} = the concentration corrected for oxygen.
C_{meas} = the concentration uncorrected for oxygen.
X = the volumetric oxygen concentration in percentage to be corrected to (8 percent for recovery furnaces and 10 percent for lime kiln, incinerators, or other devices).
Y = the measured 12-hour average volumetric oxygen concentration in percent.

5.2.4.2. Moisture Correction -

If both the stack gas and calibration gas are analyzed on the same basis (dry or wet) then no further correction is needed. However, if one is on a dry basis and the other is on a wet basis, then the following correction applies:

$$\text{Monitor span} = \frac{(\text{calibration gas, ppm})\ (1 - B_{ws}) \times 100}{(\text{monitor response to calibration gas, ppm})}$$

in which B_{ws} = moisture content of the stack gas

$$\text{Source } TRS_{corr,\ dry} = \frac{(\%\ \text{response})\ (\text{monitor span})}{(1-B_{ws})}$$

When O_2 is measured on a wet basis, then

$$TRS_{corr,\ dry} = \frac{(\%\ \text{response})\ (\text{monitor span})}{(1-B_{ws},\ \text{source gas})}$$

When O_2 is measured on a dry basis, then

$$TRS_{corr,\ dry} = TRS_{dry} \left[\frac{20.9 - \%\ O_2\ \text{Specified}}{20.9 - \dfrac{\%\ O_2\ \text{measured}}{1 - B_{ws}}} \right]$$

When dry calibration gas is used to calibrate a TRS monitor and the gases pass through a wet SO_2 scrubber, the reported data is on a dry basis and does not need to be corrected for the moisture content of the gases leaving the scrubber.

5.3 COMMERCIALLY AVAILABLE TOTAL REDUCED SULFUR CONTINUOUS EMISSION MONITORS

As discussed in the previous section, the continuous monitoring of total reduced sulfur from Kraft pulp mills involves different methods of extraction and analysis. Some systems require moisture removal while others don't. Some systems convert the TRS to SO_2 and then analyze the resultant SO_2 as TRS, while others measure the TRS directly after column separation.

Table 5.9 lists the manufacturers who provide TRS systems to the pulp and paper industry. However, not all systems listed in Table 5.9 have been used in the field or are commercially available as a package system. Table 5.10 summarizes those systems with reference to experience categories, while Table 5.11 discusses the operation and maintenance of those systems with field experience.

Following Table 5.11 are descriptions of the operating principle of all commercially available TRS CEM systems.

TABLE 5.9
COMMERCIALLY AVAILABLE TOTAL REDUCED SULFUR CONTINUOUS EMISSION MONITORS

Company Name Address and Phone	Compounds Measured	Methods of Measurement	Monitor System Identification	Probe			Conditioning System			Transfer Linefer	SO_2 Removal	Combustion Furnace	Pump	Pollutant Analyzer	Diluent Analyzer
				Temp	Filter	Pump	Condenser	Vaporizer	Dryer						
Anacon P.O. Box 416 South Bedford Street Burlington, MA 01803	SO_2, H_2S, NO_x	UV Radiation	Anacon Monitor 207	Stack	In-stack	-	No	No	Perma-pure Dryer	-	Water cooled Barton Filter	Quartz chips	Heated	UV Differential Absorption	Zirconium Oxide Technique
	CO, CO_2, H_2S,	Infrared Radiation	Anacon Monitor 206												
Applied Automation, Inc. Pawhuska Road Bartlesville, OK 74004 (918)676-6141	TRS	Gas Chromatograph	Optichrom® 2100	Stack	Inertial Filter	Steam Eductor	Air Cooled	Yes	Perma-pure Dryer	Heated	None	None	Heated	Gas Chromatography	-
Bendix Corporation (new combusion engineering) Environmental & Process Instruments Division P.O. Drawer 831 Lewisburg, WV 24901 (304)647-4358	TRS, O_2	Gas chromatograph with flame photometric detection	Bendix TRS Emissions Monitoring System	Stack	Inertial Filter	Eductor	-	Yes	Perma-pure Dryer	Not Heated	None	None	Heated Enclosure	Gas Chromatography Titration	Zirconium Oxide Technique
Candel Industries Limited 9865 West Sanich Road P. O. Box 2500 Sidney, B. C. Canada V8L-4C1 (604)656-0156	TRS, SO_2, O_2, CO, NO_x	Transducer (continuous)	Extractor Model EP-3000	Heated	Coalescing	Eductor	0-5°/C	No	-	Heated	Dry SO_2 Scrubber	Quartz Tube	Heated Enclosure	Electrochemical Transducer	-
	TRS, SO_2, O_2, CO, NO_x	Transducer (one to six samples at a time)	Extractor Series EC1000 Source Samplers												
	TRS, SO_2, O_2, NO_x, CO, Cl, H_2S, Combustibles	Transducer (electrochemical reaction detection)	Dynalyzer Series 3000 (Portable)												
Charlton Technology, Inc. P. O. Box 26818 San Diego, CA 92126 (619)578-5040	TRS, (also SO_2, NO_x, O_2, CO_2, and Hydrocarbons)	FPD/Fluorescent	Model CM-6000 and DRYSTAK Conditioner (Models SC-10, SO1016, 16)	Stack	Stainless Steel By-pass	Air Eductor	No	No	Perma-pure Dryer	Not Heated	Wet Scrubber	Quartz Tube	Heated Enclosure	Fluorescent or Flame Photometric	Zirconium Oxide Technique

TARLE 5.9 (Continued)
COMMERCIALLY AVAILABLE TOTAL REDUCED SULFUR CONTINUOUS EMISSION MONITORS

Company Name Address and Phone	Compounds Measured	Methods of Measurement	Monitor System Identificaiton	Probe			Conditioning System			Transfer Linefer	SO_2 Removal	Combustion Furnace	Pump	Pollutant Analyzer	Diluent Analyzer
				Temp	Filter	Pump	Condenser Dryer								
Columbia Scientific Industries Corporation P. O. Boxz 9908 Austin, TX 78766 (800)531-5003 (512)257-5181 (in Texas)	Conditioning TRS, SO_2, NO_x CO_2, hydrocarbon	Contitioning Flame Photometric (SO_2)	CSI-Model 85210 SA285E	Stack	None	Ejector Pump	Dilution Principle			Not heated	Dry Scrubber	None	Heated Enclo-sure	Flame Photometric	Zirconium Oxide
Thermo Electron Corp. 108 South Street Hopkinton, Mass. 01748 (617)435-5321	TRS SO_2, NO, CO_2	Dilution Probe with Flame Photometric Detector	Model 200 System TRS Monitor	Stack	None	Ejector Pump	Dilution Principle			Not heated	Dry Scrubber	None	Heated	Flame Photometric	Zirconium Oxide
ITT Barton Instruments 900 S. Turnbull Canyon Rd. P. O. box 1882 City of Industry, CA 91749	TRS, O_2, Opacity	Coulometric titration	ITT Barton Model 411 TRS Monitor (Kraft Mill CEM)	Stack	In-Stack	-	Refrigeration			Not Heated	Wet Scrubber	Quartz Tube	Heated Enclo-sure	Coulometric Titration	
Lear Siegler, Inc. 74 Inverness Drive East Englewood, CO 80110 (404)763-8003	TRS	Differential Absorption	TRS Monitor	Stack	Out-of-Stack	Air Eductor			Air Cooled	Heated	None	Quartz Tube	Heated Enclo-sure	Dual Beam Differential Absorption	Electro-chemical Cell
Sampling Technology, Inc. P. O. Box 8 Waldron, AR 72958	TRS	Thermal Oxidation UV Fluorescent	Model 100 TRS System	Stack	Inertial Filter	Steam Eductor	Air Cooled	-	Perma-pure	Not Heated	Dry Scrubber with moisture	Quartz tube	Heated Enclo-sure	Fluorescence Spectroscopy	Electrochemical Fuel Cell
Theta Sensors, Inc. 17635-A Rosland St. City of Industry, CA 91748 (213)965-1539	TRS, SO_2, O_2	Transducer (electrochemical) reaction detection)	Model 7600 Automatic TRS Analyzer	Stack	Inertial Filter	Air Eductor	-	-	Perma-pure	Not Heated	o Dry scrubber o Liquid scrubber	Dilution with quartz tube	Not Heated	Electrochemical Transducer	Electrochemical Transducer
Tracor Atlas, Inc. 9441 Baythorne Dr. Houston, TX 77041 (713)462-6116	H_2S H_2S	Lead Acetate Tape optoelectronic detection	722R H_2S Analyzer Model 825R	Stack	In-stack		Dilution Principle			Not Heated	Liquid Scrubber	Dilution with quartz tuhe	Heated	Lead acetate optoelectronic	
Western Research 1313-44 Avenue North East Calgary, Alberta Canada T2E6L5 (403)276-8806	TRS	Gas Chromatograph	Model 800 TRS Analyzer	Stack	In-stack		-	-	-	Heated	Gas Chromatography	None	Air Aspirator	Dual flame photometric	-

TABLE 5.10

TRS CEM EXPERIENCE CATEGORIES

I. Available TRS Systems with Field Experience

- Sampling Technology Inc.
- ITT Barton Instruments
- Bendix Corporation
- Western Research Corporation
- Charlton Technology Inc.

II. Available TRS Systems Without Field Experience

- Applied Automation Inc.
- Candel Industries Limited
- Lear Siegler Inc.

III. Systems Not Commercially Available As A Package System

- Anacon
- Columbia Scientific Inc.
- Thermo Electron Corporation
- Theta Sensors, Inc.
- Tracor Atlas, Inc.

TABLE 5.11
OPERATION/MAINTENANCE EXPERIENCE OF FIELD INSTALLED TRS MONITORING SYSTEMS

Company Name Address and Phone	Compounds Measured	Methods of Measurement	Monitor System Identification	Operation and Maintenance Problems	Installations				Manhours Per Month
					None	0-10	11-25	>25	
ITT Barton Instruments 900 S. Turnbull Canyon Rd. P. O. box 1882 City of Industry, CA 91749	TRS, O_2, Opacity	Coulometric titration	ITT Barton Model 411 TRS Monitor (Kraft Mill CEM)	o Maintaining constant flow o Cell Replacement o Negative Response to TRS concentrations o Corrosion o Carbon intense o Detector cell sensitive to temperature and pressure variations o Pump o Electrical failure o Cell and scrubber solutions o Excess drift after changing cell				X	40
Sampling Technology, Inc . P. O. Box B Waldron, AR 72958	TRS	Thermal Oxidation UV Fluorescent	Model 100 TRS System	o Condenser problems o Probe plugging o Leaks in Teflon ferrules o Dry SO_2 scrubber and flow control o Eductor problems o Value ticking o Permeation system o Large dry air requirement				X	45
Tracor Atlas, Inc. 9441 Baythorne Dr. Houston, TX 77041 (713)462-6116	H_2S		722R H_2S Analyzer Model 825R	o Refilling of acetic acid bubbler o Replacement of sensitized tape and H_2 tank biweekly o Unit is flow sensitive o Upstream/downstream pressure sensitive		X			
	H_2S	Lead Acetate Tape optoelectronic detection							
Western Research 1313-44 Avenue North East Calgary, Alberta Canada T2E6L5 (403)276-8806	TRS	Gas Chromatograph	Model 800 TRS Analyzer	o Complex o Software problems		X			
Bendix Corporation (new combustion engineering) Environmental & Process Instruments Division P.O. Drawer 831 Lewisburg, WV 24901 (304)647-4358	TRS, O_2	Gas chromatograph with flame photometric detection	Bendix TRS Emissions Monitoring System	o Eductor problems o Perma pure dryer failures o Stainless steel inertial filter element replacement due to corrosion from lime kiln o Corrosion o Software problems o Higher degree of technical experience required o Auto valving failure o Moisture		X			50
Candel Industries Limited 9865 West Sanich Road P. O. Box 2580 Sidney, B. C. Canada V8L-4C1 (604)656-0156	TRS, SO_2, O_2, CO, NO_x	Transducer (continuous)	Extractor Model EP-3000	o Limited Field Experience	X				N/A
	TRS, SO_2, O_2, CO, NO_x	Transducer (one to six samples at a time)	Extractor Series EC1000 Source Samplers						
	TRS, SO_2, O_2, NO_x, CO, Cl, H_2S, Combustibles	Transducer (electrochemical reaction detection)	Dynalyzer Series 3000 (Portable)						
Charlton Technology, Inc. P. O. Box 26818 San Diego, CA 92126 (619)578-5040	TRS, (also SO_2, NO_x, O_2, CO_2, and Hydrocarbons)	FPD/Fluorescent	Model CM-6000 and DRYSTAK Conditioner (Models SC-10, S01016, 16)	o Hydrocarbon cutter replacement		X			N/A

5.3.1 Candel Industries Limited

Candel Industries Limited (CIL) has developed a highly specialized system for monitoring TRS compounds in the presence of SO_2. In essence, a source sample is extracted from the source, conditioned and analyzed for SO_2 by an electrochemical transducer. As illustrated in Figure 5.28, the basic components of the system are:

- Probe/conditioning system;
- SO_2 scrubber and TRS converter system; and
- Electrochemical sensor.

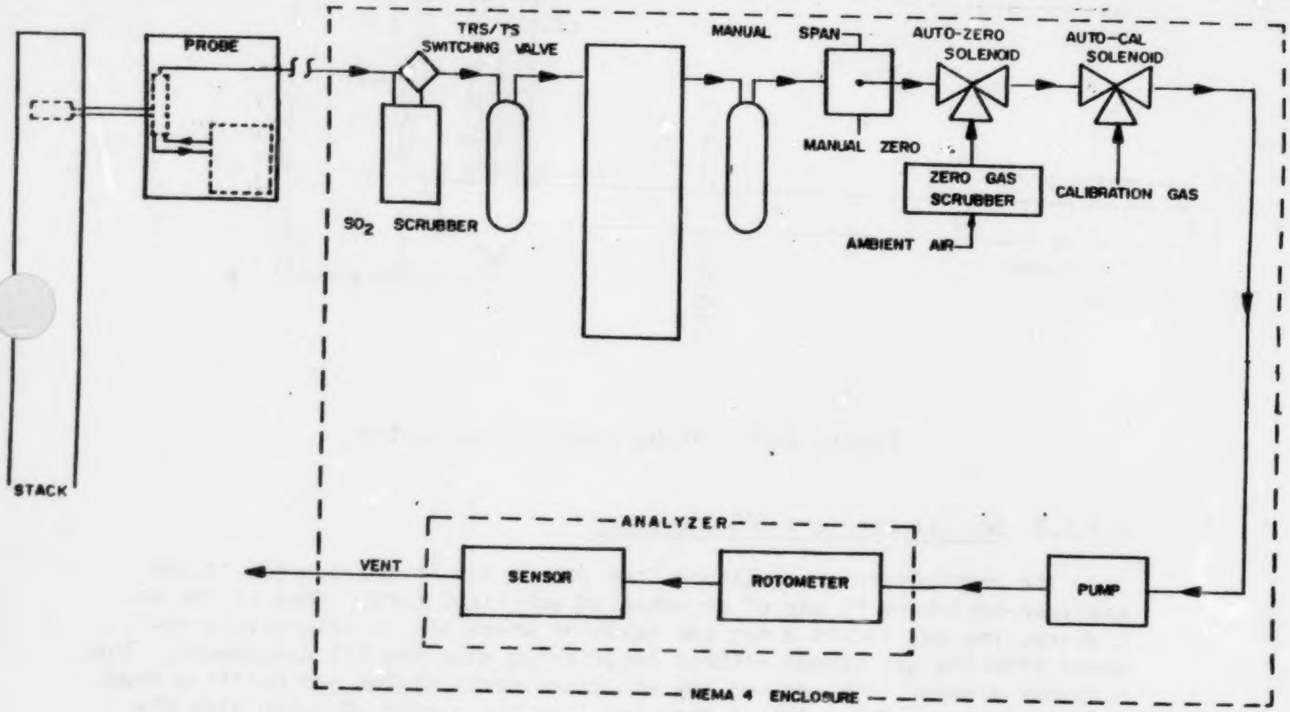
STACK
PROBE
TRS/TS
SWITCHING VALVE
SO2 SCRUBBER
MANUAL
SPAN
MANUAL ZERO
AUTO-ZERO
SOLENOID
AUTO-CAL
SOLENOID
ZERO GAS
SCRUBBER
AMBIENT AIR
CALIBRATION GAS
ANALYZER
VENT
SENSOR
ROTOMETER
PUMP
NEMA 4 ENCLOSURE

Figure 5.28. Candel Industries TRS System.

5.3.1.1 Probe/Conditioning Sustem -

The probe/conditioning system consists of a titanium probe, an air cooled condenser with condensate trap, and an eductor for sample gas extraction. As illustrated in Figure 5.29, the sample gas is extracted, by the eductor (E), through the probe to the air cooled condenser (CC). There, the gas stream is cooled between 0-5°C. Condensibles are condensed and collected in the condensate trap (Co). By way of a second pump located in the instrument module, a sample portion of the sample gas (S) is extracted from the larger gas stream for subsequent analysis.

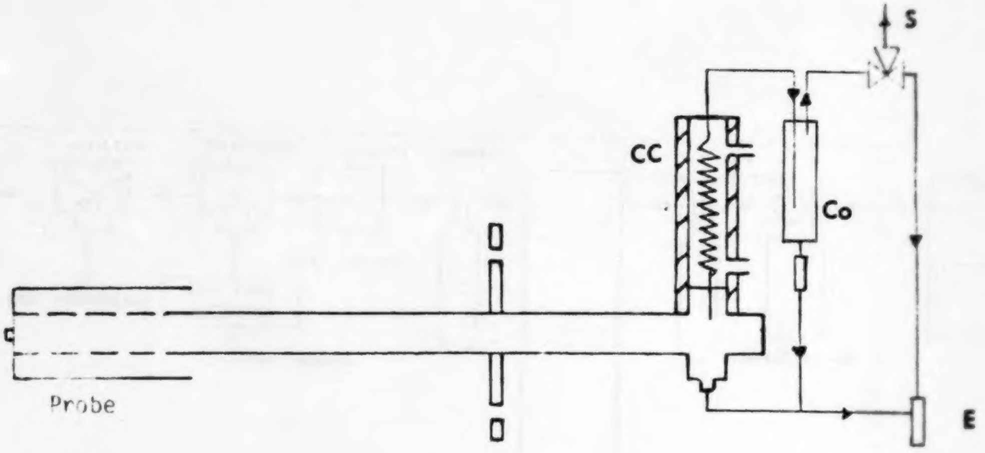

Figure 5.29. Probe/Conditioning System.

5.3.1.2 SO_2 Scrubber and TRS Converter -

The particulate and moisture free gas stream is transported to the analyzer enclosure by way of an unheated umbilical cord. Once at the enclosure, the gas enters a dry bed scrubber where SO_2 is selectively removed from the gas stream without interfering with the TRS components. The scrubber element also removes any entrained particulates and moisture from the sample gas. The moisture absorbed from the sample gas also aids the SO_2 scrubber action. Once SO_2 is removed from the gas stream, the stack gas then passes through an oxidizer which converts the TRS components to SO_2. The sample gas is then pumped, by a continuous duty corrosion resistant pump, to the analyzer.

5.3.1.3 Electrochemical Sensor -

As illustrated in Figure 5.30, the CIL TRS analyzer utilizes the polarographic principle of detection for measuring SO_2 (TRS converted) in the gas stream.

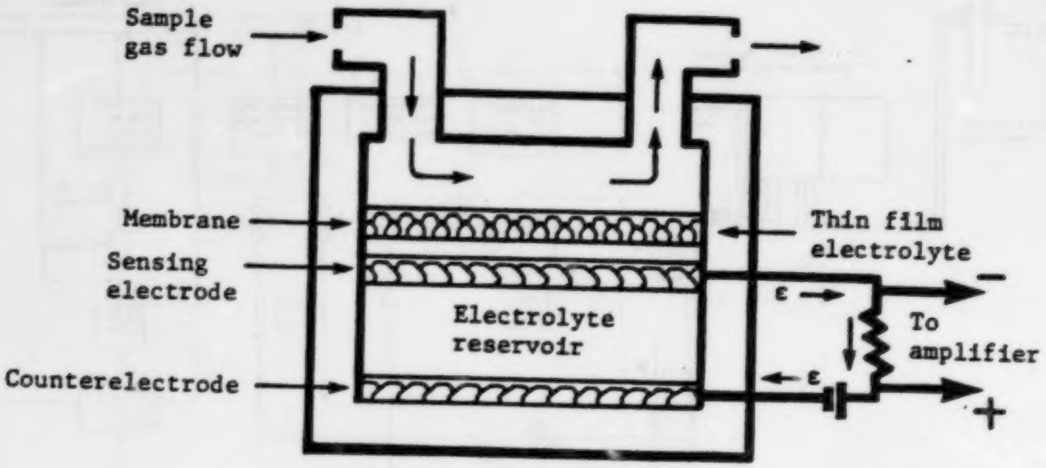

Figure 5.30. Polarographic Principle.

In operation, the SO_2 in the flue gas is drawn into a detection cell, where a selective semi-permeable membrane allows only SO_2 to diffuse through to the porous sensing electrode. The pollutant undergoes electro-oxidation, releasing electrons according to the following chemical reaction:

$$SO_2 + 2H_2O \longrightarrow SO_4^{-2} + 4H^+ + 2e^-$$

The net result is a release of electrons to the counter-electrode by means of the electrolytic reservoir. The flow of electrons is directly proportional to the initial SO_2 concentration, consequently the initial concentration of TRS.

5.3.2 Charlton Technology Model CM-6000 Continuous TRS Monitoring System

The Charlton Technology Model CM-6000 Continuous TRS Monitoring System consists of a probe assembly, sample conditioner, sample transport and analyzer module. The analytical technique involves extracting a sample from the source, conditioning that sample and analyzing for TRS as SO_2. Sample gas is extracted from the stack by means of an air eductor. The sample is withdrawn through a probe assembly to the sample conditioner where it is filtered and moisture removed by a permeation dryer. The sample is then transported from the sample conditioner, by way of heat trace line, to the analyzer module containing the dilutor, SO_2 scrubber, TRS oxidizer and SO_2 analyzer. Figure 5.31 displays the major components of the Model CM-6000 Continuous TRS Monitoring System.

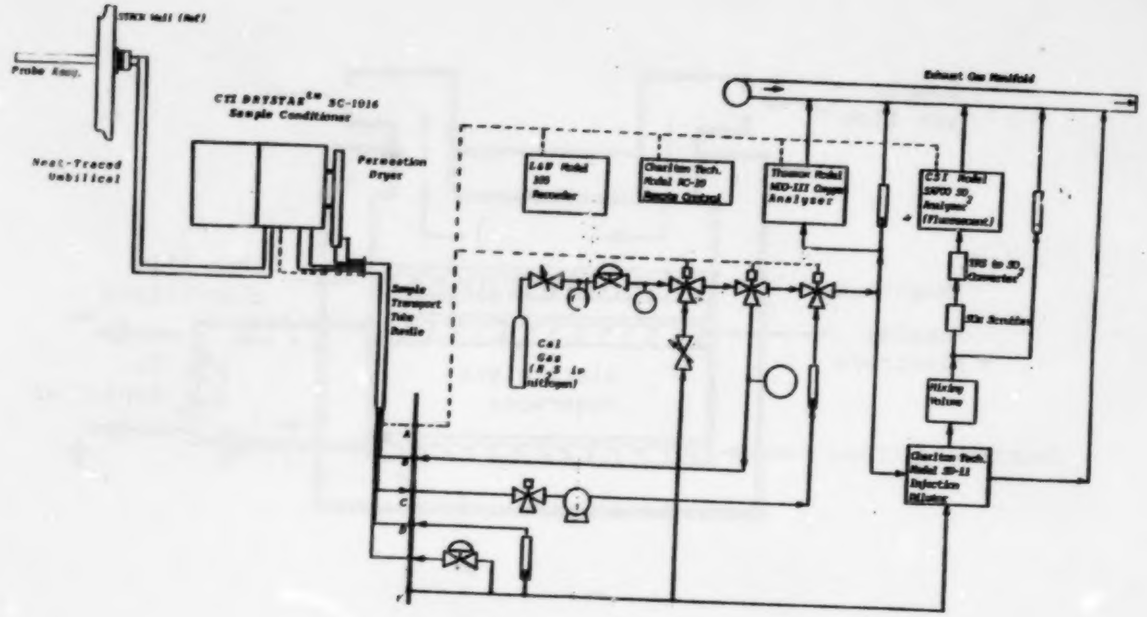
Stack Wall (Ref)
Probe Assy.
CTI DRYSTAR™ SC-1016
Sample Conditioner
Heat-Traced
Umbilical
Permeation
Dryer
Sample
Transport
Tube
Bundle
Cal
Gas
(H2S in
nitrogen)
L&N Model
100
Recorder
Charlton Tech.
Model RC-20
Remote Control
Thermox Model
WDG-III Oxygen
Analyzer
CSI Model
SA700 SO2
Analyzer
(Fluorescent)
TRS to SO2
Converter
SO2 Scrubber
Mixing
Volume
Charlton Tech.
Model ID-11
Injection
Dilutor
Exhaust Gas Manifold
A
B
C
D
E

Figure 5.31. Charlton Technology Model CM-6000 TRS System.

5.3.2.1 Probe/Sample Conditioning Assembly -

The probe assembly is typically a 3/4" corrosion-resistant alloy unit about 3 feet long. The probe is mounted on the source with a mounting hub. A locknut on the mounting hub permits the operator to slide the probe body into the stack to any desired depth. The probe is designed for a single point extraction. Because the probe is attached to the sample conditioner with a heat trace line, it can be removed easily for periodic service or inspection.

The gas sample is extracted from the stack by means of a venturi-type air eductor. The sample is brought into the heated fiberglass sample conditioner enclosure and maintained at a temperature above sample dew point. A side-stream withdraws a small portion of the gas by a diaphragm pump through a sintered stainless steel bypass filter (to remove particulate down to 1 micron or less). This technique is termed inertial filtration.

The clean, filtered sample is then introduced to a permeation dryer, externally mounted on the side of the module, where moisture is removed to achieve a dew point below ambient temperature. This eliminates the requirement for a heat-traced sample line between the sample conditioner and the analyzer in the control room. Figure 5.32 displays the components of the probe/sample conditioner system.

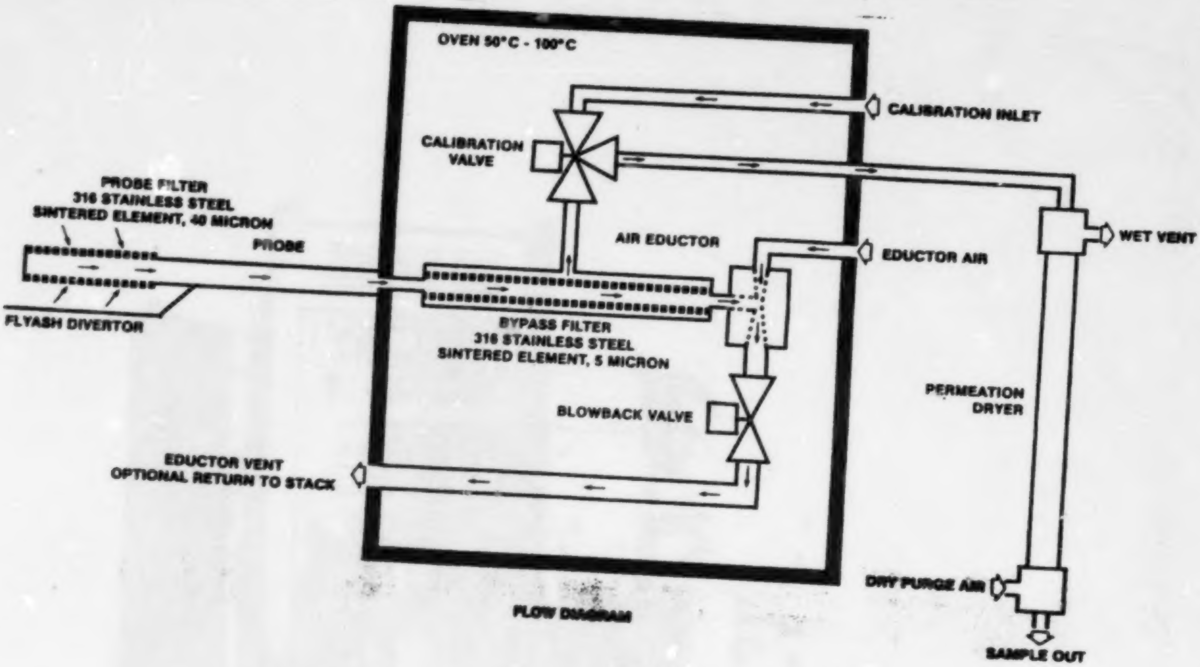
OVEN 50°C - 100°C
CALIBRATION INLET
CALIBRATION VALVE
PROBE FILTER 316 STAINLESS STEEL SINTERED ELEMENT, 40 MICRON
PROBE
AIR EDUCTOR
EDUCTOR AIR
WET VENT
FLYASH DIVERTOR
BYPASS FILTER 316 STAINLESS STEEL SINTERED ELEMENT, 5 MICRON
PERMEATION DRYER
BLOWBACK VALVE
EDUCTOR VENT OPTIONAL RETURN TO STACK
DRY PURGE AIR
FLOW DIAGRAM
SAMPLE OUT

Figure 5.32. Probe/Conditioning System.

5.3.2.2 Sample Transport Line -

From the conditioning system, the moisture and particulate free gas stream is transported, by positive pressure from the diaphragm pump, to the sample control module by a 7-bundle sample transport line. The 7 bundle transport line involves:

Tube #	Function
1	AC Power to Sample Conditioner
2	AC Switching
3	Calibration Gas
4	Sample Line
5	Purge Air
6	Eductor Air
7	Spare

5.3.2.3 Instrumentation Module -

The instrumentation module contains the diluter module, the dry-bed SO_2 scrubber, the TRS to SO_2 converter, the CSI fluorescence SO_2 analyzer, the Thermox oxygen analyzer and recorder/data processor. As shown in Figure 5.32, the undiluted sample gas flows from the sample conditioner to the analyzer where it is divided into two streams. The major portion of the sample (dry and undiluted) flows to the oxygen analyzer for analysis while the smaller flow enters the sample diluter where a precision dilution is made with zero air. From the diluter, the sample passes through a dry-bed SO_2 scrubber, then to a TRS oxidizer to convert TRS to SO_2 then finally to the fluorescence SO_2 analyzer for analysis. Figure 5.33 displays the instrument rack containing all monitoring systems associated with the TRS system. The amount of SO_2 present, as indicated by the fluorescent SO_2 analyzer, is directly proportional to the original concentration of TRS present in the stack gas.

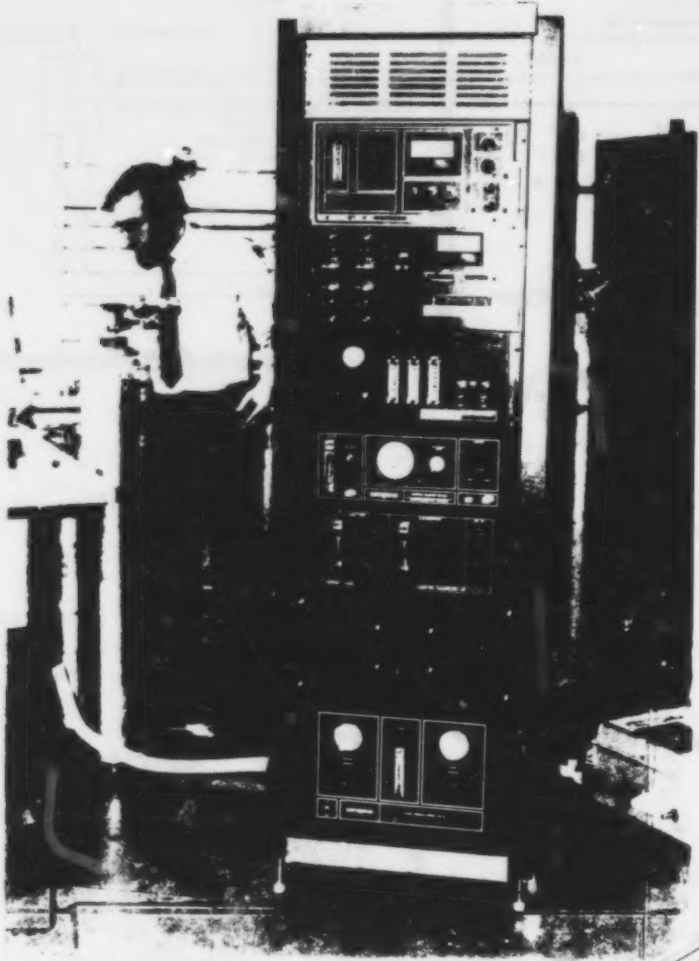

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Figure 5.33. Charlton Technology TRS Instrument Rack.

5.3.3 Columbia Scientific Industries

The Columbia Scientific Industries (CSI) dilution probe operates on the principle of extracting a gas sample from the source, diluting that sample with clean, dry instrument air and analyzing the gas components with EPA certified ambient air monitors. The CSI stack gas analyzer comprises two parts:

- The in-situ sample conditioning/dilution probe; and
- Meloy Labs flame photometric or fluorescence SO_2 analyzer.

5.3.3.1 Conditioning/Dilution Probe

The main objective of the conditioning/dilution probe is to extract a precise sample volume from the source, remove particulate and dilute the source sample to ambient concentration, all at stack conditions.

Figure 5.34 illustrates the major components of the conditioning/dilution probe.

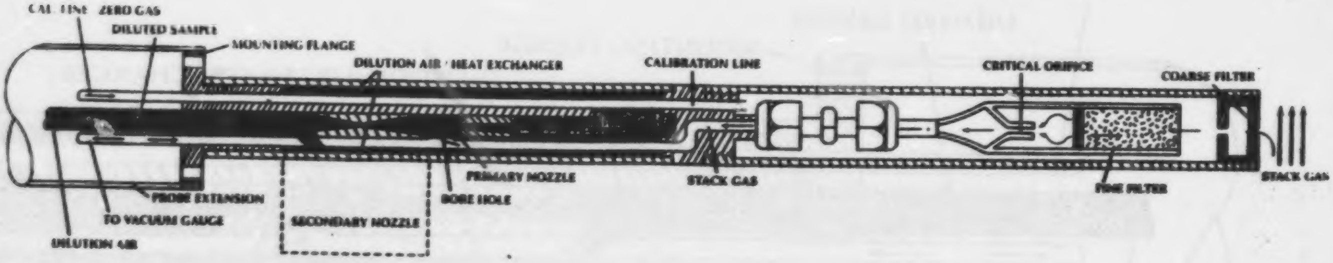

CAL LINE
ZERO GAS
DILUTED SAMPLE
MOUNTING FLANGE
DILUTION AIR / HEAT EXCHANGER
CALIBRATION LINE
CRITICAL ORIFICE
COARSE FILTER
STACK GAS
PRIMARY NOZZLE
STACK GAS
FINE FILTER
PROBE EXTENSION
BORE HOLE
TO VACUUM GAUGE
SECONDARY NOZZLE
DILUTION AIR

Figure 5.34. CSI Dilution Probe.

In operation, stack gas is first drawn through a fine filter and metered by a critical orifice, as shown in Figure 5.35.

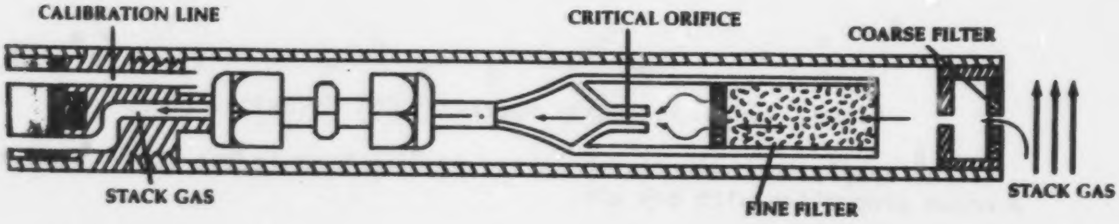

CALIBRATION LINE
CRITICAL ORIFICE
COARSE FILTER
STACK GAS
STACK GAS
FINE FILTER

Figure 5.35. Fine Filter/critical Orifice of CSI Dilution Probe.

A vacuum is drawn on the stack continuously, through the filter and critical orifice, by a small eductor pump mounted behind these components (Figure 5.36). Pressurized dilution air creates a vacuum in the space between the primary and secondary nozzle causing the movement of the stack gas through the system.

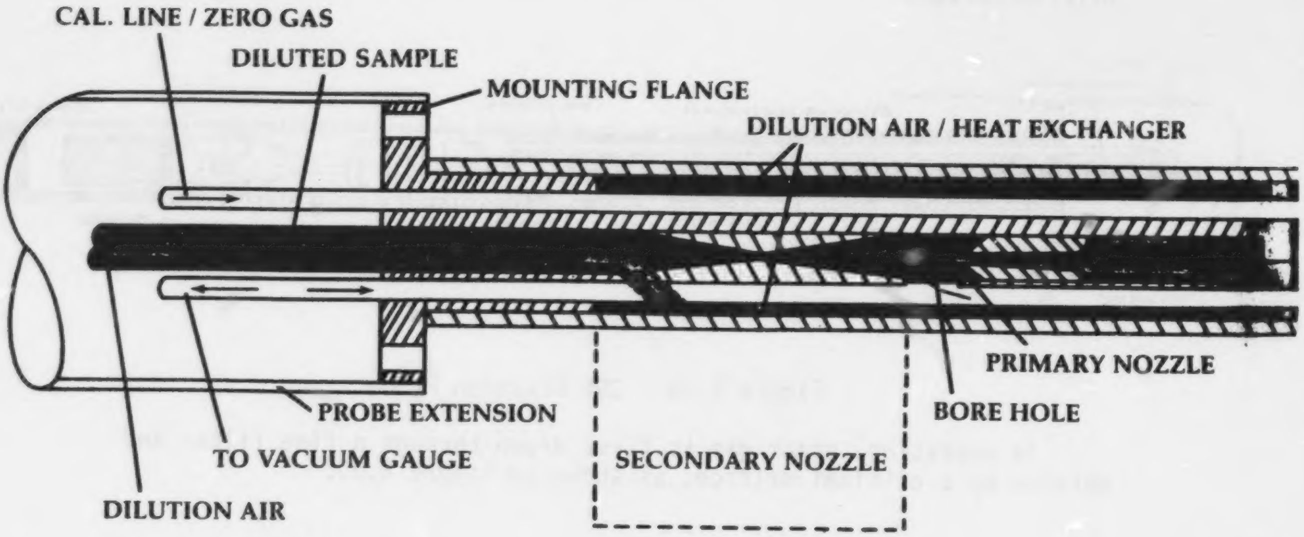

CAL. LINE / ZERO GAS
DILUTED SAMPLE
MOUNTING FLANGE
DILUTION AIR / HEAT EXCHANGER
PRIMARY NOZZLE
BORE HOLE
PROBE EXTENSION
TO VACUUM GAUGE
SECONDARY NOZZLE
DILUTION AIR

Figure 5.36. Secondary Nozzle of CSI Dilution Probe.

The sample is then diluted in the ejector pump in the stack probe to a known proportion with dry air.

The diluted gas stream, 100:1 ratio, is then fed through unheated sample lines to a dry SO_2 scrubber and then to the ambient continuous emission monitors, located off the stack, for subsequent analysis by flame photometry.

When utilizing the dilution probe technique, the measured pollutant concentration is on a wet basis.

5.3.3.2 CSI Analyzer

In flame photometry, the sample is excited to luminescence by introduction into a flame. A hydrogen flame is used in the flame photometric method to excite the sulfur atom. The excited atom will, in turn, emit light in a band of wavelengths centered at about 394 nm, which is then detected by a photomultiplier tube, as shown in Figure 5.28.

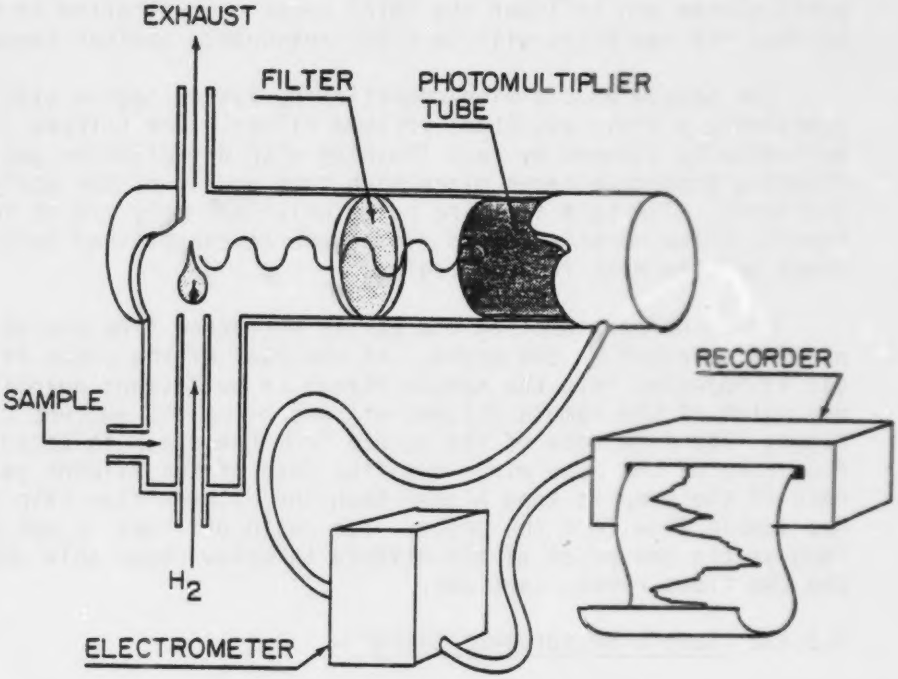


Figure 5.37. CSI Flame Photometric Detector.

A disadvantage of flame photometric analyzers is the required hydrogen for the flame. Facilities that have strict regulations concerning the use of hydrogen and hydrogen cylinders may find it inconvenient to utilize this method. For this reason, fluorescence spectroscopy has been used for the detection of SO_2 in the gas stream more often than flame photometry.

5.3.4 Tracor Atlas, Inc. Total Reduced Sulfur Continuous Measurement System

The Tracor Atlas Total Reduced Sulfur measurement system is based on the chemical reaction between lead acetate and hydrogen sulfide to produce black lead sulfide. The total reduced sulfur measurement system is divided into two subsystems: (1) sample acquisition and conditioning, and (2) sample measurement.

5.3.4.1 Sample Acquisition and Conditioning System -

The two constituents of the stack atmosphere that can interfere with TRS measurements are particulates and water vapor. The Tracor Atlas TRS sample acquisition and conditioning system is designed to eliminate particulates and to lower the water vapor concentration in the sample gas so that its dew point will be under reasonable ambient temperatures.

The sample acquisition/conditioning system begins with a probe containing a stainless steel fritted filter. The fritted filter is periodically cleaned by back flushing with dry dilution gas. The back flushing procedure takes place each tape update of the analyzer or every 3 minutes. The back flushing pulse will last only 1/4 of the tape movement time to allow normal forward flow to be re-established before tape movement stops and the next reading begins.

Under normal sampling the gas is extracted from the stack by a pump placing a vacuum on the probe. At the back of the probe is a tee. A dry gas is injected into the sample stream in sufficient quantity to drop the dew point of the sample diluent mixture below the ambient temperature range. The flow rate of the sample from the stack is essentially the flow rate of the pump minus the flow rate of the diluent gas. The flow rate of the pump is kept higher than the diluent flow rate to maintain a net sample flow from the probe. The ratio of flows is not critical as long as the dew point of the mixture is below reasonable ambient condition and the flows remain constant.

5.3.4.2 Sample Measurement System -

The conditioned stack gas sample is then introduced into a barium acetate SO_2 scrubber where SO_2 is removed while allowing all other sulfur species to remain in the sample gas. The gas exiting from the scrubber is mixed with hydrogen and introduced into a tube furnace where all remaining sulfur species are hydrogenated to H_2S.

The reacted gas then exits the furnace and enters the H_2S analyzer where the H_2S concentration of the gas is determined. The H_2S concentration is directly proportional to the amount of total reduced sulfur in the stack gas sample.

The H_2S analyzer is based on the lead acetate detection principle. The analyzer has no known interferences. Very high sensitivity is achieved by using a stopped-tape method, detecting the darkening of the tape opto-electronically, and then differentiating the signal with respect to time. The output of the analyzer is the rate of change of darkness of the tape which is directly proportional to the H_2S concentration for a given set sample flow rate. The method is capable of measuring H_2S in samples in the low parts per billion range.

The H_2S sample flows into the reaction window (Sample Chamber) where it passes over an exposed surface of lead acetate impregnated paper, as shown in Figure 5.38.

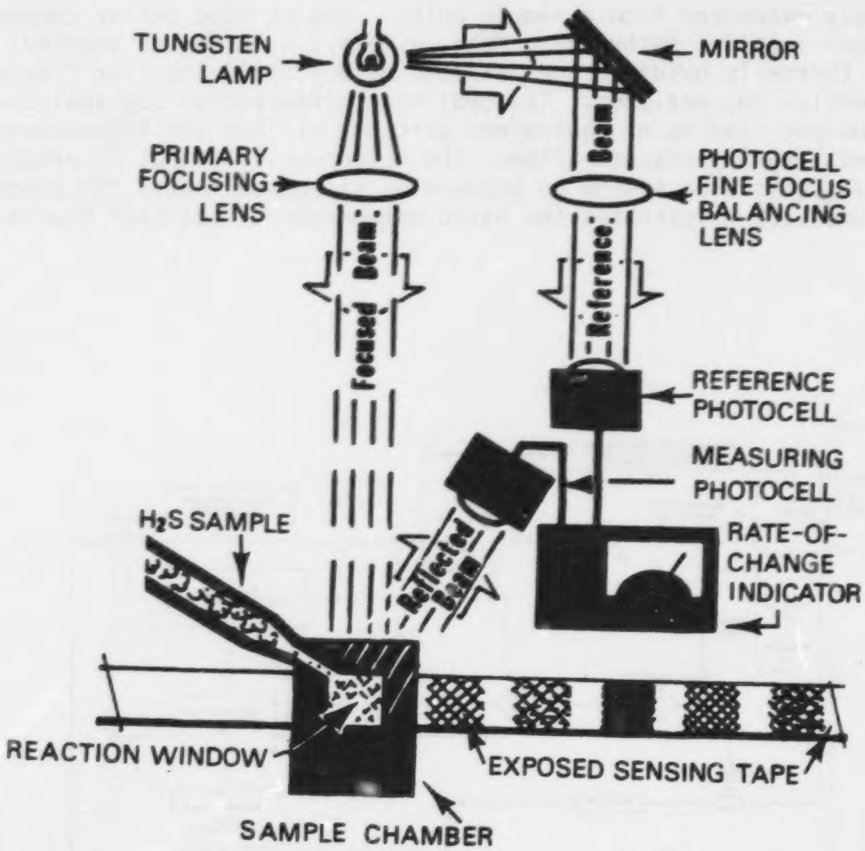

TUNGSTEN LAMP
MIRROR
PRIMARY FOCUSING LENS
Beam
PHOTOCELL FINE FOCUS BALANCING LENS
Focused Beam
Reference
REFERENCE PHOTOCELL
MEASURING PHOTOCELL
RATE-OF-CHANGE INDICATOR
H₂S SAMPLE
Reflected Beam
REACTION WINDOW
EXPOSED SENSING TAPE
SAMPLE CHAMBER

Figure 5.38. Sample Measurement System; Impregnated Lead Acetate Paper.

The lead acetate paper darkens due to the presence of H_2S, as lead sulfide is formed. The rate of darkening of the exposed tape is proportional to the H_2S concentration in the stack gas. The amount of darkening of the tape is monitored by a patented optical system.

As illustrated in Figure 5.29, light from a 14 volt DC tungsten lamp is focused into the viewing area by a primary lens. The light then strikes the sensing tape and is reflected to the measuring photocell. Simultaneously, the light from the same 14 volt DC tungsten lamp is reflected from a mirror and focused to produce a reference beam for the reference photocell. Signals from the measuring and reference photocells are sent to the rate reading electronics to produce a meter deflection. The difference between these two signals is directly proportional to the TRS originally present in the stack gas stream.

5.3.5 Lear Siegler Continuous TRS Monitoring System

For continuous monitoring of TRS, Lear Siegler utilizes an extractive measurement system whereby a representative sample of stack gas is continuously extracted from a sample point. The reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) are thermally oxidized and analyzed as SO_2 utilizing Lear Siegler's differential SO_2 analyzer. The dual beam differential SO_2 analyzer produces an output reading of equivalent part per million TRS independent of the coexisting SO_2 concentration. The differential signal is processed by a data acquisition system to produce an oxygen-corrected TRS concentration. Figure 5.39 illustrates the basic components of the Lear Siegler TRS system.

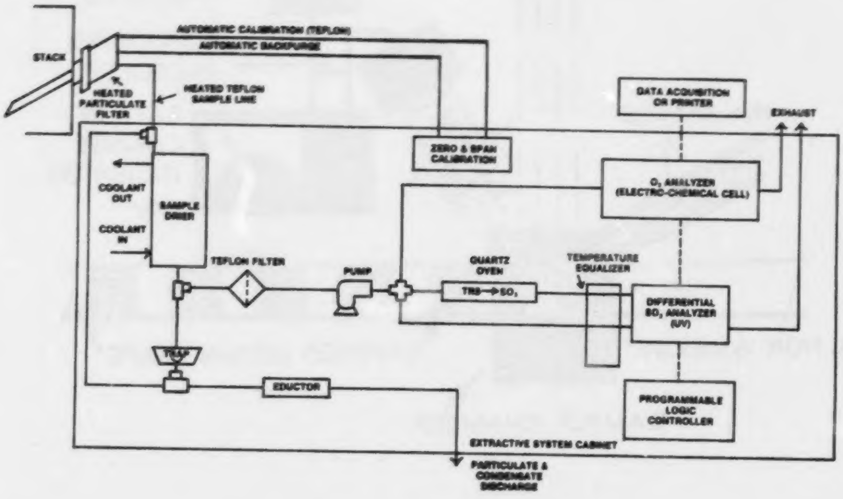

AUTOMATIC CALIBRATION (TEFLON)
AUTOMATIC BACKPURGE
STACK
HEATED PARTICULATE FILTER
HEATED TEFLON SAMPLE LINE
DATA ACQUISITION OR PRINTER
EXHAUST
ZERO & SPAN CALIBRATION
O_2 ANALYZER (ELECTRO-CHEMICAL CELL)
COOLANT OUT
SAMPLE DRIER
COOLANT IN
TEFLON FILTER
PUMP
QUARTZ OVEN
$TRS \rightarrow SO_2$
TEMPERATURE EQUALIZER
DIFFERENTIAL SO_2 ANALYZER (UV)
TRAP
EDUCTOR
PROGRAMMABLE LOGIC CONTROLLER
EXTRACTIVE SYSTEM CABINET
PARTICULATE & CONDENSATE DISCHARGE

Figure 5.39. Lear Siegler TRS CEM System.

5.3.5.1 Probe and Primary Filter Assembly -

Unique in its design, the probe assembly includes an electrically heated filter chamber, located outside the mounting flange. This allows the filter to be maintained without removing the probe from the gas stream. The filter location also eliminates pluggage of the filter by direct impact of particulates or water droplets on the filter. For ease of maintenance, separate gas connections for sample extraction, backpurge, and calibration gas injections are incorporated in the filter chamber design.

The probe is mounted sloping downward into the stack. The open end of the probe is cut at an angle to create an opening away from the gas flow. This eliminates direct impingement of particulates, enabling the filter backpurge system to maintain a clear sample tube in most cases. The straight-through design of the sample tube allows blockage to be cleared with a ramrod without removing the probe from the gas stream.

For TRS monitoring applications, the probe includes a Teflon lining and a non-reactive, sintered glass heated filter to remove particulates without loss of TRS components. Check valve inlets are provided for both calibration gas and high pressure backpurge air, both automatically sequenced from the analyzer cabinet. Manual valves are provided for periodic backflush of probe with either water or air.

5.3.5.2 Sample Transport Line -

The Lear Siegler system includes heat-traced teflon®-lined sample transport lines from the probe location to the analysis cabinet. Self-limiting, heattraced lines operate without any external temperature control or voltage limiting devices. The sample gas stream temperature is maintained above the dew point throughout its run, thereby preventing condensation and resultant loss of TRS in transport.

5.3.5.3 Sample Drier -

The sample is dried to a dew point corresponding to the coolest ambient temperature in the gas transport system by means of a simple air to air cooling system. For maximum cooling efficiency, the gas flows through multiple teflon tubes which are in direct contact with the ambient air. The condensate exits the bottom of the heat exchanger to an automatic liquid drain, while the dried sample is drawn out for final filtration and analysis. For lime kiln applications, a sample drier may be located in a heated enclosure at the probe to remove moisture before entering the heated sample line.

5.3.5.4 Thermal Oxidation Furnace -

An electrically heated quartz tube thermal oxidation furnace is provided to oxidize the sample stream reduced sulfur compounds to SO_2 prior to analysis. Sample temperature in this oxidizer is approximately 750°C and residence time is maintained so that further oxidation to SO_3 does not occur. Due to the relatively small amount of TRS and the typically high content of O_2, the TRS compounds are completely oxidized without substantially altering the O_2 content of the sample gas stream. A coiled tube heat exchanger following the oxidizer is provided to cool the sample gas prior to analysis.

5.3.5.5 Gas Prime Movers -

Low flow rate air eductors operated by compressed air draw the sample from the stack and transport the sample stream to the analyzer cabinet. A teflon lined diaphragm pump moves the gas sample through the thermal oxidation furnace, secondary filters and to the analyzers. A back pressure regulator and calibrated rotameter are provided for flow control to the analyzers. As a result, the analyzers are operated at near atmospheric pressure.

5.3.5.6 Dual Beam Differential SO_2 Analyzer -

The SO_2 analyzer provides dual beam differential measurement of SO_2, which produces an output reading of equivalent parts per million of TRS independent of the coexisting SO_2 concentration. An ultra-violet light source is directed through the measurement cell, which is divided into measurement and reference sections. The light beam passing through the cell is gated alternately through the measurement and reference sections by a continuously rotating chopper. The light reaching the detector at the opposite end of the cell is attenuated by the SO_2 present in each section of the cell. The gas stream extracted from the process is flowed continuously through the reference section of the cell, providing a reference SO_2 level equal to the process SO_2 concentration. At the same time, the extracted gas stream is oxidized by the thermal oxidation furnace where the TRS is oxidized to SO_2 and the original SO_2 in the extracted gas stream remains. This gas stream continuously flows through the measurement section of the analyzer. The detector, therefore, measures a varying light intensity as the light beam is alternated between the measurement and reference sections, and the difference in the two measurements is proportional to the SO_2 produced by oxidizing the TRS compounds. Rotating at 1600 revolutions per minute, the chopper generates two test periods in each rotation and gates the light beam through the reference and measurement sections of the cell. During each test period, zero and gain of the instrument are automatically adjusted to compensate for the effects of line voltage variation, lamp and detector aging, and varying concentrations of background SO_2.

5.3.5.7 Microprocessor Controller -

The microprocessor controller accumulates continuous concentration data and provides both one and twelve-hour averages. Diluent (O_2) correction is also provided and required violation summaries are generated. Recorders and/or printers can be located remotely for operator convenience.

Automatically sequenced calibration is initiated by the microprocessor controller and accomplished at the probe location through the introduction of known concentrations of H_2S and O_2 span gases. Calibration gas is delivered to the probe via a separate Teflon line thus allowing the sample line to be used only for transport of the sample gas. This assures fast response time to changes in sample TRS concentration. Further, the measurement of calibration gas injected at the probe ensures a valid evaluation of the entire measurement system including the normal sample line. All components function under normal operating conditions during the calibration check thereby verifying normal operation. The automatic calibration cycle normally occurs once every twenty-four hours.

5.3.6 Theta Sensors, Inc. Model 7600 TRS Monitor

The Model 7600 consists of several individual components designed for and integrated into the overall system. The main components of the system are the sample probe, pump, sample line, sulfur dioxide scrubber, TRS oxidizer, oxygen and sulfur dioxide analyzers, and the data logger.

The heart of the monitor is an electrochemical transducer which selectively measures SO_2.

Source monitoring requires the sample to be acquired from the source and conditioned so as to be compatible with the requirements of the monitor. These tasks must be accomplished without degrading the sample's integrity. The complexity of the sampling system, therefore, depends primarily on the monitor requirements. TSI instruments require a clean gas, free of particulates, and a dry gas free of entrained water with a dew point less than the monitor's ambient temperature.

5.3.6.1 Sample Probe -

The analysis begins with the extraction of the sample from the source by a probe/conditioner system. Within the probe, the high speed sample passes through a tubular (inertial) filter. A small portion of this sample is drawn radially through the porous filter wall at a velocity so low that the inertia of solid and liquid particulates will be too high to curve through the wall of the filter. The resulting sample is free of interfering particulates, but will be saturated with water vapor. To prevent water from condensing in the lines the sample is immediately dried using a permeation dryer. The cool, clean, and dry sample is transported to the rest of the system.

5.3.6.2 Sample Pump -

Since the sample now has a very low water content, it is pumped without further condensation. A stainless steel and inert plastic diaphragm pump provides a sample flow of approximately two liters per minute. The pump is located at the probe so that the balance of the system will be under pressure to eliminate small leaks in the sample line.

5.3.6.3 Sample Line -

Because the sample has very low moisture content, the sample lines are not heated. Almost any line material can be used which will not degrade the sample. TFE or FEP may be used as well as polypropylene or 316 stainless steel.

5.3.6.4 Sulfur Dioxide Scrubber -

Theta sensors utilize several methods for removal of SO_2, including both solid and liquid techniques. Although the solid scrubbers are attractive because of their apparent ease of use, they have limited capacity, and must be replaced or serviced frequently. Theta sensors use a number of liquid scrubbers, including saturated sodium bicarbonate and citric acid/sodium citrate. Both of these liquid scrubber solutions are non-toxic and non-corrosive. From the SO_2 scrubber, the sample goes to the TRS oxidizer.

5.3.6.5 TRS Oxidizer -

Before entering the oxidizer, the stack sample is diluted to ensure enough oxygen present for oxidation.

The diluted sample is heated to 100°C in a quartz reaction tube. The result is a complete conversion of the reduced sulfur compounds to SO_2.

5.3.6.6 Detector

The Theta Sensors transducer utilizes the chemical reaction occurring between a gas and a charged electrode to produce a current flow which is measured in an electronic circuit. The transducer is often referred to as an electrochemical transducer.

The transducer is divided into two major sections. The upper section provides a flow path for the sample gas while the lower section is the reaction chamber. The two sections are separated by a permselective membrane and sealed by the compression of an "O" ring and gasket. A snap ring fastens the assembly together.

The permselective membrane accomplishes three important tasks. First, the proper choice of membrane allows the gas specie under investigation to diffuse through it more rapidly while inhibiting the passage of interfering gases, thus providing a degree of specificity. Second, the membrane reduces the amount of reactive gas reaching the sensing electrode, thereby increasing the life of the transducer. Third, the membrane seals the electrolyte in the body allowing the transducer to be operated in any position.

As the sample gas diffuses through the membrane, the gas specie under investigation is either oxidized or reduced by the sensing electrode which is maintained at a fixed potential in relation to the counter-electrode. This potential is unique to each gas specie.

The oxidation or reduction of the gas specie, i.e., the gain or loss of electrons, causes a flow of electrons between the two electrodes. This current is measured in the external electronic circuitry. The current produced is directly proportional to the concentration of the specie in the sample gas, thereby assuring linearity over the entire dynamic range. Accordingly, a direct relationship exists between reduced sulfur compounds in the gas stream and current produced at the detector.

135

5.3.6.7 Oxyen and Sulfur Dioxide Analysis -

The oxygen is measured in the sample stream just prior to the addition of the diluent air. The measurement is made with an electrochemical sensor.

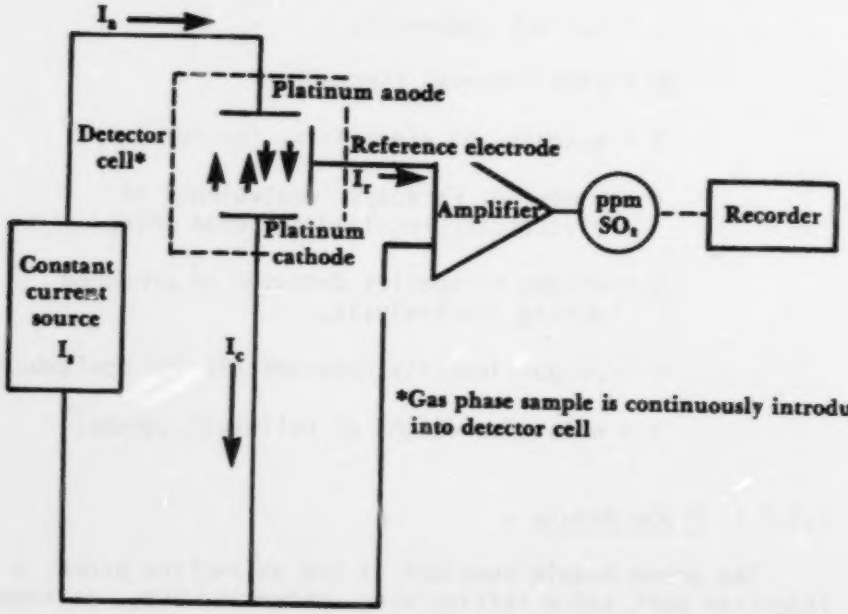
5.3.6.8 Data Logging

The computer provides for all self-testing and data logging needs of the system. The TRS measurements and any corrections for oxygen concentration are based on a dry sample, and need not be corrected for the moisture content of the stack. Consequently, the data logger produces all concentrations in units of the standard.

5.3.7 ITT - Barton Titrator

The ITT-Barton Model 411 recording sulfur analyzer consists of three distinct components: (1) probe module; (2) sample module and (3) titration module. A stack gas is extracted from the source, conditioned and analyzed coulometrically through an oxidation-reduction reaction. The measurement is performed by adding a known amount of reagent to a sample until the reactive components are exhausted. By measuring the current required to maintain a constant concentration of reagent, a concentration of pollutant entering the module can be calculated.

Coulometric analysis uses the electrical change generated by the reduction of bromine in a titration cell to measure the SO_2 gas concentration in the measurement stream. The titration cell consists of three electrodes arranged to form two functional pairs. One pair acts as the bromine generating electrode and the other pair serves as a sensing and control electrode. The anode is common to both pairs of electrodes. Figure 5.40 demonstrates the arrangement of these electrodes.



*Gas phase sample is continuously introduced into detector cell

Figure 5.40. ITT Barton Titrator.

The operation of the cell involves maintaining a constant concentration of bromine in the electrolytic solution. As SO_2 is introduced into the cell, the bromine concentration is reduced by the following reaction:

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2Br^- + 2H^+$$

The equilibrium of the electrolytic solution (Br_2/Br^-) is disturbed and this change is sensed by the basic amplifier. Changes in the concentration of bromine in the cell electrolyte cause the sensing electrode to vary the current supplied to the input of the electrical circuit. This current provided by the control module causes the production of bromine at the sensing electrode to return the cell to its original equilibrium or end-point condition. The amount of current required to maintain this equilibrium (end-point) is proportional to the concentration of SO_2 (and consequently TRS) in the sample gas. The following reactions occur at the individual electrodes:

$$2\ Br - 2e^- \rightarrow Br_2 \text{ (anode)}$$

$$Br_2 + 2e^- \rightarrow 2\ Br \text{ (cathode)}$$

By measuring the current across the cell from these combined reactions, the concentration of SO_2 in the sample gas can be determined through Faraday's Law. Faraday's Law states that one gram-equivalent of material is reduced by one Faraday of electricity according to the following reaction:

$$(I)\ dt = Q = \frac{nwF}{m}$$

Where:

I = current (amperes);

dt = time interval (seconds);

Q = quantity of electricity (coulomb);

n = number of Faradays (equivalent) of electricity required per gram mole;

w = weight of species consumed or produced during electrolysis;

F = proportionality constant (96,487 coulombs/mole)

M = molecular weight of pollutant (grams)

5.3.7.1 Probe Module -

The probe module consists of the extraction probe, a calibration gas injection port and a refrigerated condensate trap, as shown in Figure 5.41. The gas sample is extracted (∿ 1 CFM) through the probe by a pump located in the sampling module, and transported to the condensation trap in the refrigerated lower section of the module. The refrigeration is supplied by a vortex tube cooler controlled by a thermostat-solenoid valve combination. As water is removed from the gas stream, it collects in the condensate reservoir which empties once per day. The moisture-free gas stream exits the probe module and moves through heat traced tubing to the sampling module.

5.3.7.2 Sampling Module -

The sampling module contains the high volume sample pump, back-purge equipment and the heat controller for the heat trace line. Back-purge is controlled by a timer which actuates a solenoid valve. The valve allows instrument air (regulated to 10 psi) to purge the heat-traced sample line, the probe and the condensate reservoir. While the sampling assembly is being back-purged, the sample pump draws ambient air and routes it to the analyzer for instrument zero. Figure 5.42 displays the physical arrangements of these components in the sampling module.

5.3.7.3 Titration Module -

The titration module contains the SO_2 filters, thermal oxidizer, titration cell and aspirator. Only a small fraction (250 cc/min) of the total sample from the sample module is analyzed. As demonstrated in Figure 5.43, the aspirator pulls the sample from the sampling module and into the SO_2 scrubber. The scrubber is a solution of potassium citrate/citric acid in water. Next, the SO_2-free gas stream passes through a thermal oxidation device which oxidizes all remaining sulfur compounds to SO_2. From the oxidizer unit, the gas stream enters the titration cell where SO_2 reacts with the bromine solution to produce a current. The amount of current generated is directly proportional to the SO_2 concentration (thus TRS) in the gas stream.

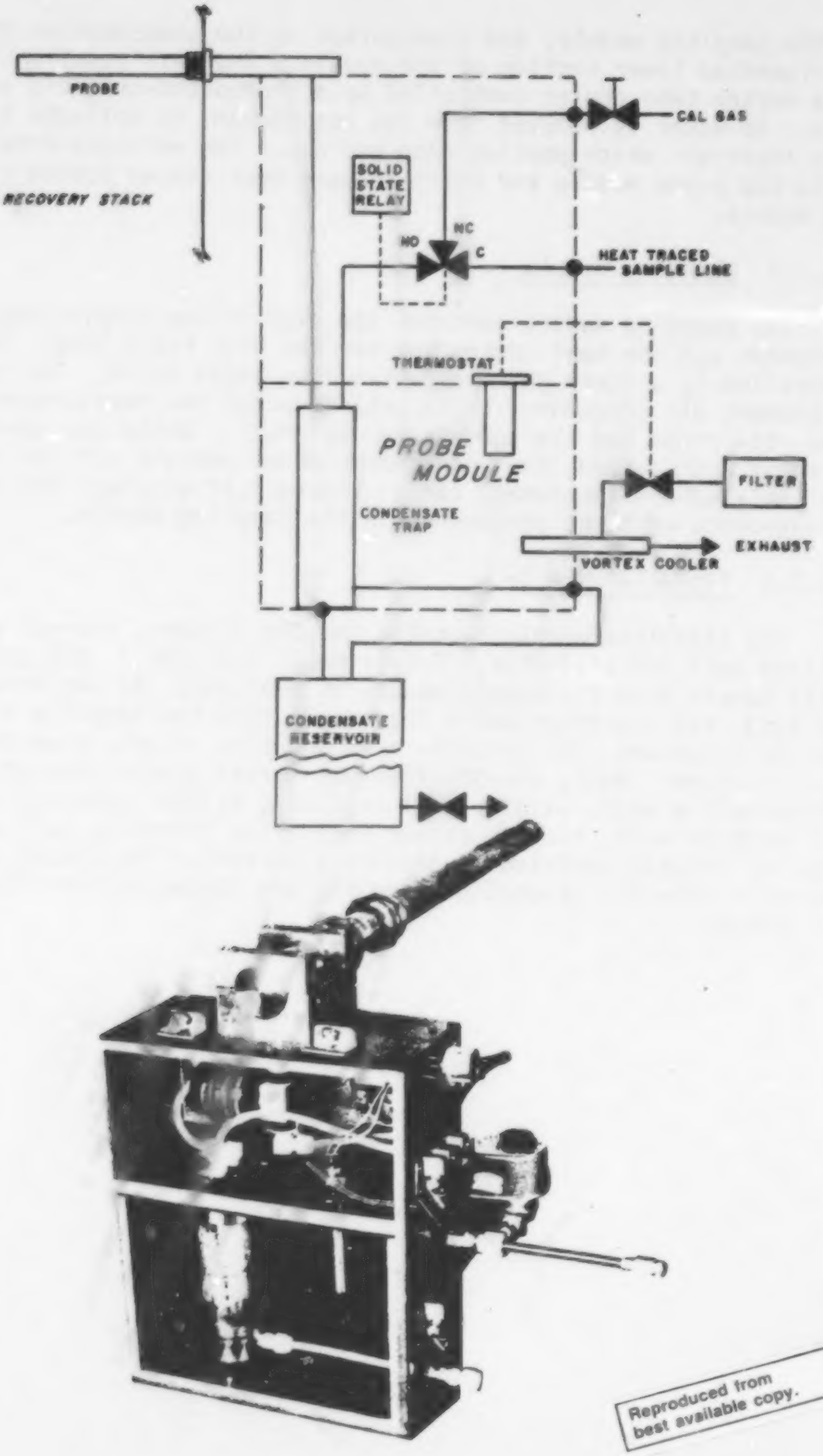

PROBE
RECOVERY STACK
CAL GAS
SOLID STATE RELAY
NO
NC
C
HEAT TRACED SAMPLE LINE
THERMOSTAT
PROBE MODULE
FILTER
CONDENSATE TRAP
EXHAUST
VORTEX COOLER
CONDENSATE RESERVOIR

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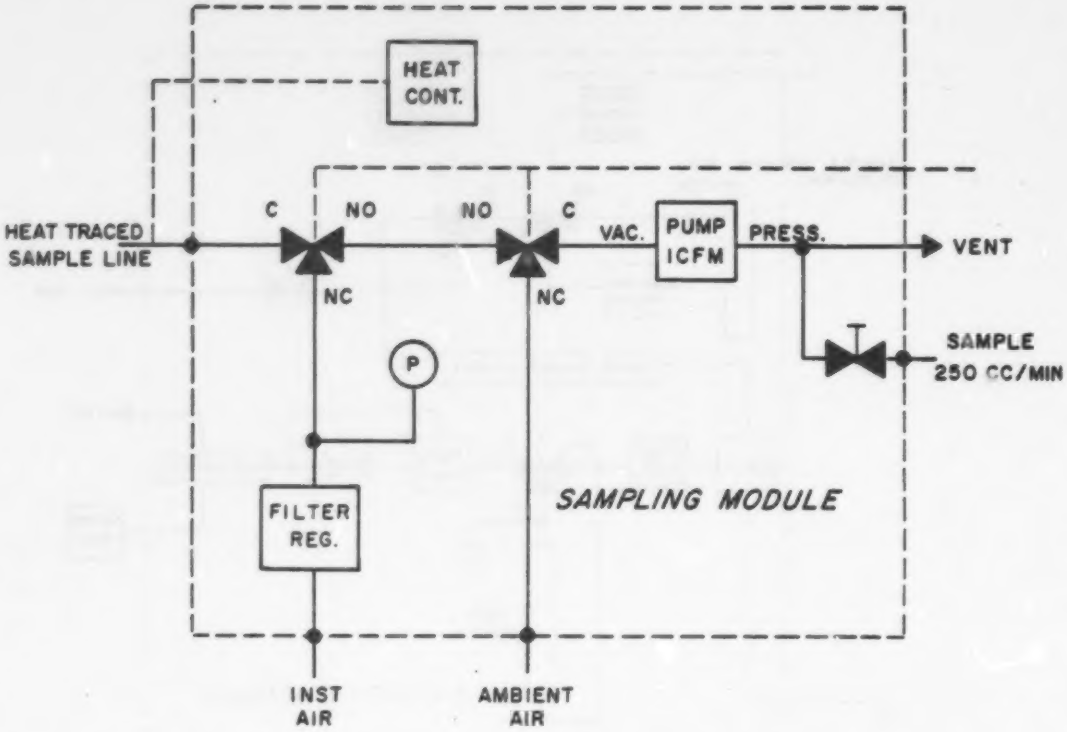
Figure 5.41. ITT Barton Probe/Extractive System.


HEAT CONT.
HEAT TRACED SAMPLE LINE
C
NO
NO
C
VAC.
PUMP ICFM
PRESS.
VENT
NC
NC
SAMPLE 250 CC/MIN
P
FILTER REG.
SAMPLING MODULE
INST AIR
AMBIENT AIR

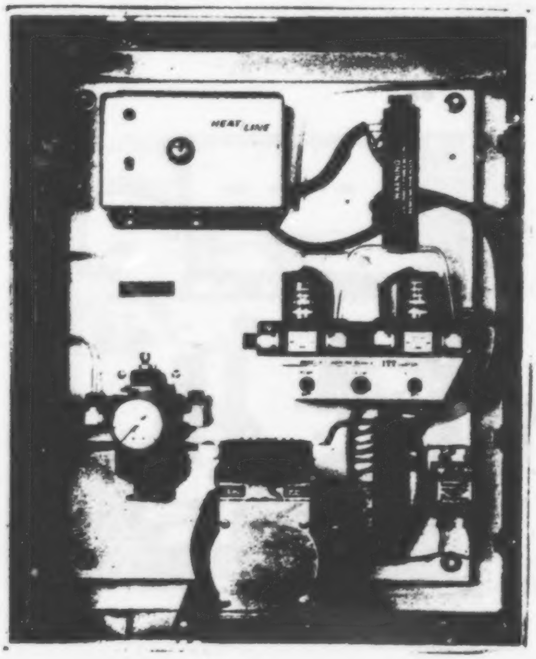


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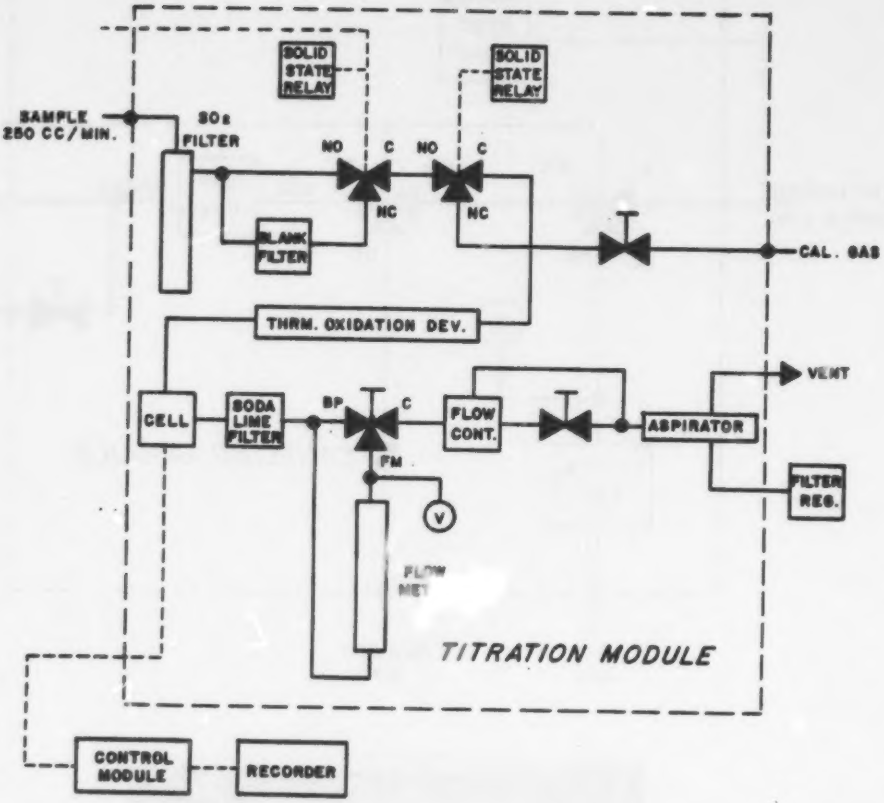
Figure 5.42. ITT Barton Sampling Module.


SOLID STATE RELAY
SOLID STATE RELAY
SAMPLE 250 CC/MIN.
SO2 FILTER
NO
C
NC
NO
C
NC
BLANK FILTER
CAL. GAS
THRM. OXIDATION DEV.
VENT
CELL
SODA LIME FILTER
BP
C
FM
FLOW CONT.
ASPIRATOR
FILTER REG.
V
FLOW MET
TITRATION MODULE
CONTROL MODULE
RECORDER

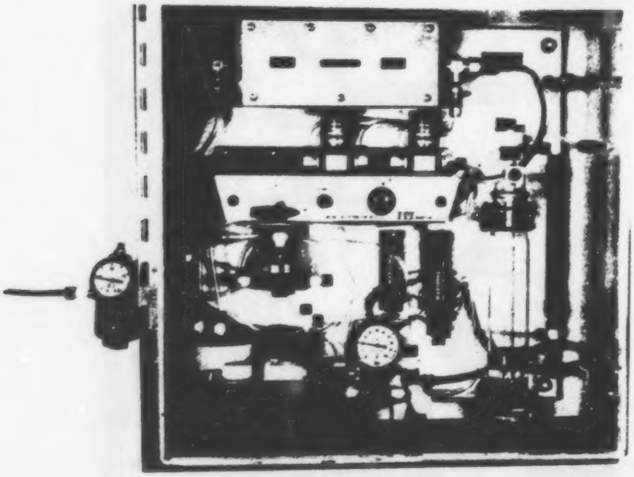


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Figure 5.43. ITT Barton Titration Module.

5.3.8 Western Research TRS CEM

The Western Research Model 800 Series Total Reduced Sulfur (TRS) analyzer consists of these basic modules:

- Probe/Conditioning System;
- Analyzer; and
- Remote Output.

The system is based upon gas chromatographic analysis for hydrogen sufide, carbonyl sulfide, dimethyl disulfide, methyl mercaptan and dimethyl sulfide. Western Research employs gas chromatography as its analytical technique because: (1) other analytical methods cannot distinguish between the different molecular forms of reduced sulfur in the gas sample; and (2) there is no alternative methodology which equally responds to all reduced sulfur compounds, thus limiting established calibration techniques. Western Research developed a process chromatographic technique to distinquish between all sulfur compounds. Since the presence of SO_2 and H_2O in the stack gas interferes with the detection of the reduced sulfur compounds they had to be either removed or separated. Consequently, Western Research developed a process TRS gas chromatography analyzer. Figure 5.44 illustrates the basic components of the Western Research Model 800 Series Total Reduced Sulfur Analyzer.

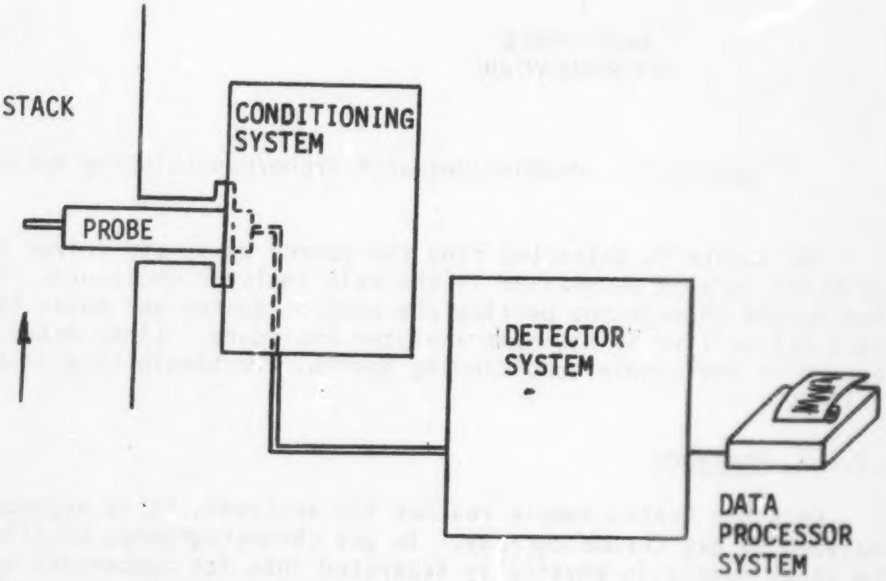


Figure 5.44. Western Research TRS CEM System.

5.3.8.1 Probe/Conditioning System -

The probe/conditioning system consists of a straight-in sampling probe and a Balston filter for particulate control, all enclosed in a heated weatherproof unit. As illustrated in Figure 5.45, the system allows for back-purge and injection of span gas as close to the probe tip as design specifications allow.

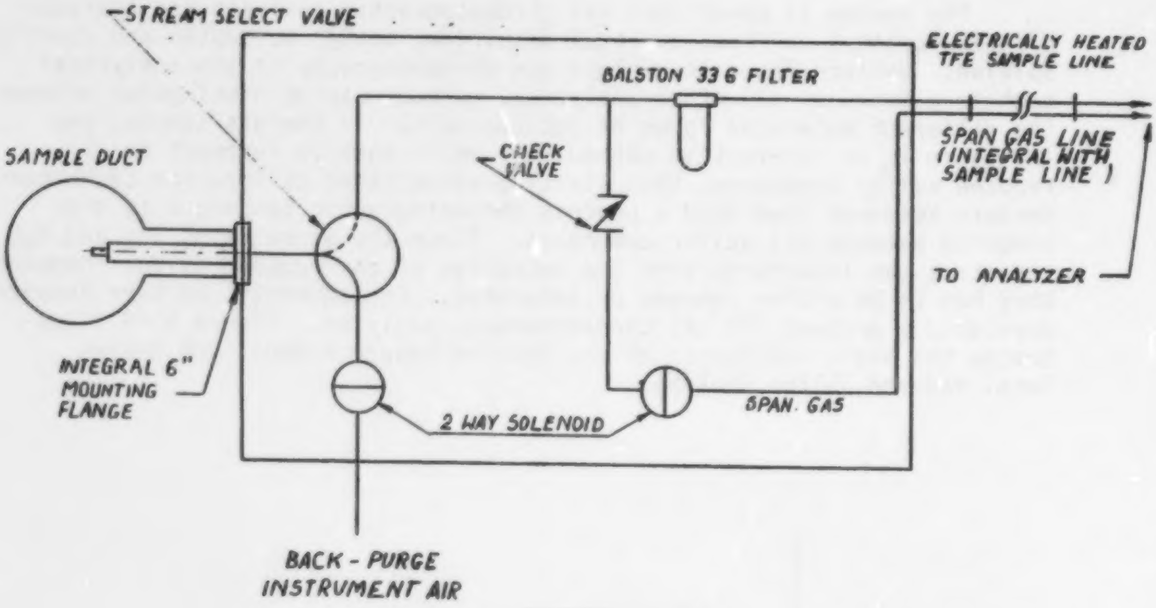

STREAM SELECT VALVE
ELECTRICALLY HEATED TFE SAMPLE LINE
BALSTON 33 G FILTER
CHECK VALVE
SAMPLE DUCT
SPAN GAS LINE (INTEGRAL WITH SAMPLE LINE)
TO ANALYZER
INTEGRAL 6" MOUNTING FLANGE
SPAN GAS
2 WAY SOLENOID
BACK - PURGE INSTRUMENT AIR

Figure 5.45. Western Research Probe/Conditioning System.

The sample is extracted from the source by an air driven teflon aspirator located downstream in the main analyzer enclosure. The sample then passes through the particulate control device and moves through heat trace teflon line to the main analyzer enclosure. Since water is not removed in the sample/conditioning system, the sample line is maintained at 120°C.

5.3.8.2 Analyzer -

Once the heated sample reaches the analyzer, it is separated and analyzed by gas chromatography. In gas chromatography, an aliquot of the stack sample is physically separated into its components by passing it through a packed column with an appropiate carrier gas. The migration rate of each component through the column is governed by its absorption affinity relative to the material of the absorber. Column materials, lengths and operating conditions are selected so that each specie of interest is separated from its neighbors and quantified by an appropriate downstream detector. As illustrated in Figure 5.46, the stack gas enters the analyzer, passes through a line filter and then into the heated sample loop where an aliquot is retained for analysis. At a select time, carrier gas is injected into the sample loop and fences the pollutants downstream through the chromatographic column to the detector.

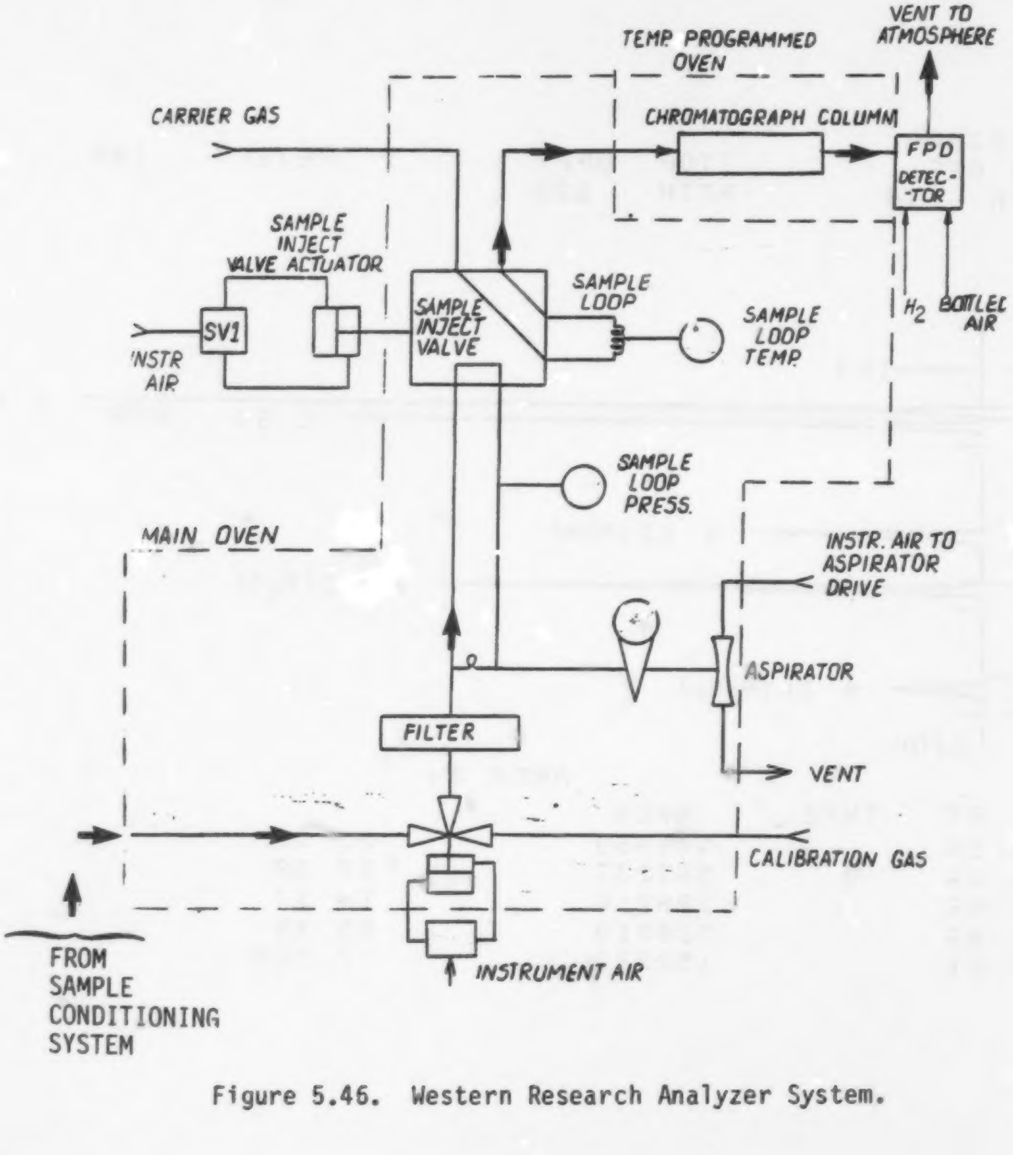
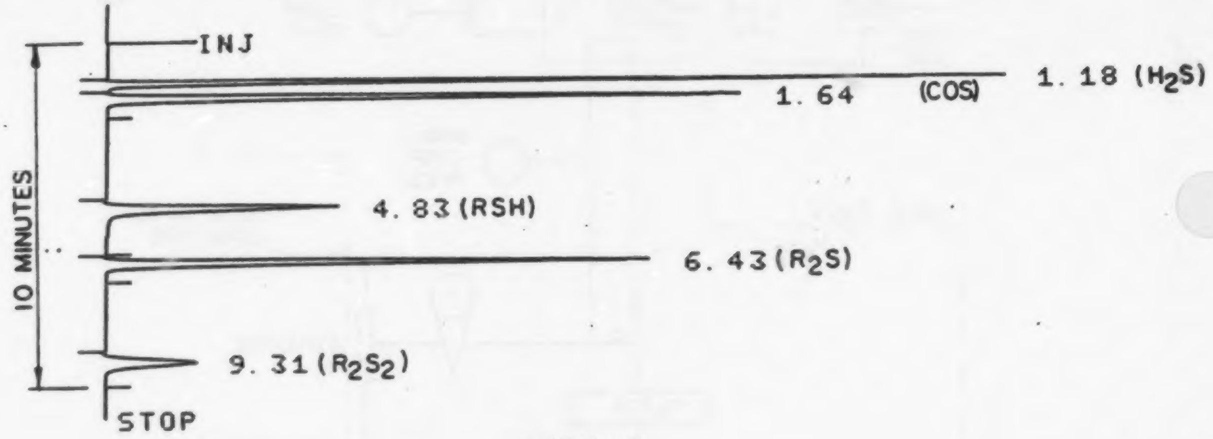

VENT TO ATMOSPHERE
TEMP. PROGRAMMED OVEN
CARRIER GAS
CHROMATOGRAPH COLUMN
FPD DETEC-TOR
SAMPLE INJECT VALVE ACTUATOR
SAMPLE INJECT VALVE
SAMPLE LOOP
SV1
INSTR AIR
SAMPLE LOOP TEMP.
H_2
BOTTLED AIR
SAMPLE LOOP PRESS.
MAIN OVEN
INSTR. AIR TO ASPIRATOR DRIVE
ASPIRATOR
FILTER
VENT
CALIBRATION GAS
FROM SAMPLE CONDITIONING SYSTEM
INSTRUMENT AIR

Figure 5.46. Western Research Analyzer System.

By virtue of the column material, temperature and physical configuration, the separation of reduced sulfur compounds in the presence of carbonyl sulfide (COS), sulfur dioxide (SO_2) and water vapor (H_2O) is accomplished. Figure 5.47 displays a typical chromatogram from a Western Research TRS CEM system.

```
HP 3380A
DLY OFF               STOP   OFF                REJECT    100
MV/M  .30             ATTN    128
```



```
                     AREA %
   RT    TYPE      AREA
 1.18             540460          25.57
 1.64     M       583233          27.59
 4.83             298716          14.13
 6.43             538910          25.49
 9.31             152572           7.218
```

Figure 5.47. Typical Chromatogram from Western Research TRS CEM System.

Once separation is accomplished by the chromatographic column, a dual flame photometric detector (FPD) quantitatively detects molecular sulfur in the presence of other components. The output response of the FPD is independent of the molecular form of the sulfur and is proportional to the square root of the sulfur mass entering the detector. The concentration of each sulfur species present in the sample is measured on a hot and wet (i.e., "as is") basis and printed out. The TRS emission is calculated as the sum of the concentrations of the reduced sulfur compounds. COS and SO_2, if present, are not included in the calculated and reported TRS emission. The system automatically checks and adjusts its calibration by means of span gas injected at the sample conditioning unit every 8 hours. Changes in calibration are printed on the hard copy output.

5.3.8.3 Remote Output -

The Remote Output processes the signal from the detector and displays final concentrations of individual TRS components of the gas stream. A typical printout of the system is displayed in Figure 5.48.

```
81/11/01        TIME   P   T  #?   H2S   COS   SO2   RSH   R2S  R2S2   TRS
PRECIP O/L      16:00 646 374 01    28    34           4.7         0.8    34
AUTO CALIBRATION CHANGE =  1.1%
GC CALIB GAS    16:13 611 374      4.7    25                             4.7
PRECIP O/L      16:25 643 373       24    29           3.1   0.8          28
PRECIP O/L      16:36 646 371       30    33           5.0                35
PRECIP O/L      16:47 645 372       42    32           3.5   1.5          47
PRECIP O/L      16:57 646 372 01    22    36           4.6                27
PRECIP O/L      17:08 645 372 01    26    40           4.1                31
PRECIP O/L      17:19 648 371 01    21    32           3.7                25
PRECIP O/L      17:29 647 371       20    27           2.8         1.2    25
PRECIP O/L      17:44 649 374 01    34    34           4.5         1.0    41
PRECIP O/L      17:54 648 371 01    30    32           5.1         0.9    37
PRECIP O/L      18:05 648 372       31    33           2.3                33
PRECIP O/L      18:15 647 371       19    33                       1.1    21
PRECIP O/L      18:26 648 372 01    42    42           4.1         1.4    49
PRECIP O/L      18:36 647 372 01    30    37           4.5         0.6    36
PRECIP O/L      18:47 648 371 01    39    42           6.0         1.3    48
PRECIP O/L      18:58 648 371 01    45    44           4.2   1.6   1.1    53
PRECIP O/L      19:08 648 371 01    51    42           5.4   1.6          58
PRECIP O/L      19:19 646 371 02    50    37                       1.1    53
```

Figure 5.48. Western Research TRS CEM System Remote Output Display.

5.3.9 Sampling Technology Incorporated TRS CEM System

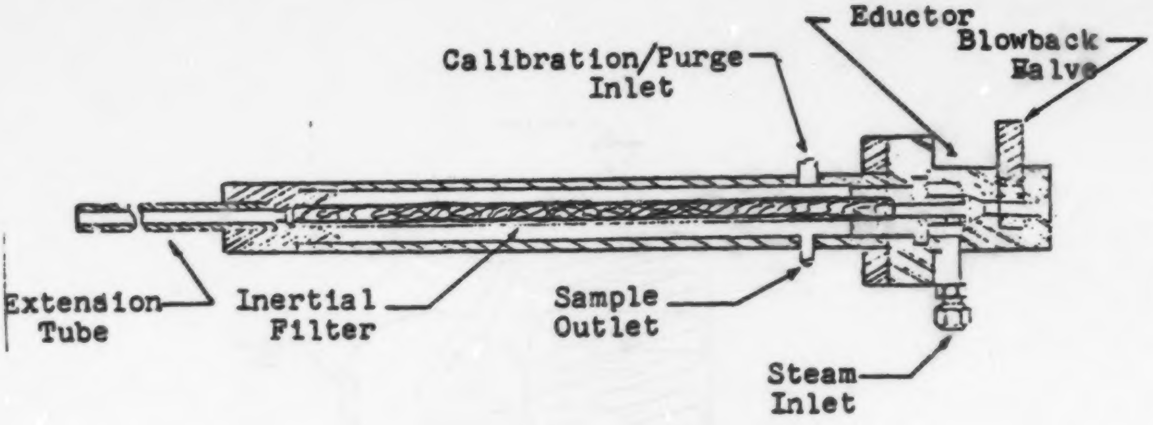
The Sampling Technology Inc. (STI) Model 100 Total Reduced Sulfur (TRS) monitoring system is designed to measure and report TRS data from lime kilns, recovery boilers, smelt tank vents and other TRS sources within the Kraft pulp mill. Like other extractive systems, it is able to monitor several sources simultaneously. The system is based on Proposed Federal Reference Method 16A where a sample is extracted, conditioned, (particulate, water and SO_2 removed), oxidized and then analyzed. Unlike proposed Federal Reference Method 16A, the STI system can incorporate either UV fluorescence or coulometric titration analysis in place of 16A wet chemical analysis.

The system consists of six functional components

- probe/conditioning system - the objective of the probe/conditioning system is to extract a sample from the source, remove moisture and transport the sample to the dilution system,
- dilution control system - the dilution control system properly dilutes the stack gas to ambient concentration,
- sulfur dioxide scrubber - similar to proposed Federal Reference Method 16A, sulfur dioxide must be removed from the gas stream prior to analysis. Consequently, a dry bed SO_2 scrubber is used,
- thermal oxidizer - the thermal oxidizer converts the remaining reduced sulfur compounds to SO_2,
- SO_2 detector - the SO_2 detector generates an electrical signal proportional to the generated SO_2 concentration in the gas stream, and
- data system - the electronic signal from the detector is received and converted to units of the standard by the data system.

5.3.9.1 Probe/Conditioning System -

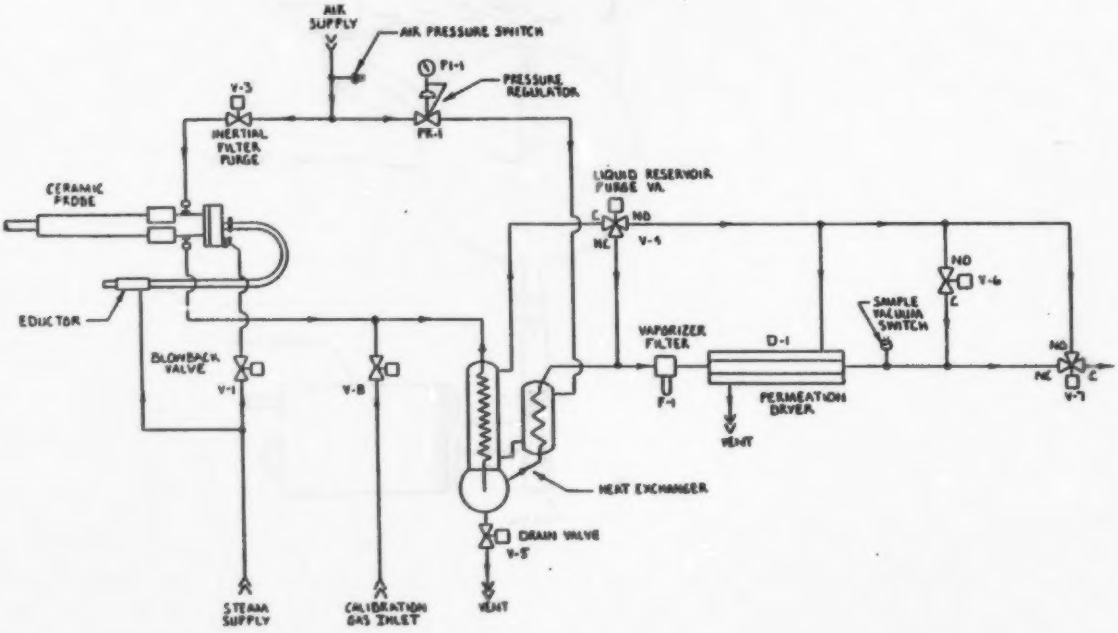
The purpose of the probe/conditioning system is to supply to the analyzer a particulate, moisture and acid free sample gas for subsequent TRS and O_2 analysis. The probe is made of a porous ceramic tube which is resistant to physical abrasion, corrosion and thermal shock (Figure 5-49). The probe configuration utilizes the principle of inertial filtration to remove large particulate matter from the sample gas. The inertial filter depends on the acceleration of the stack gas to critical velocity through the center of a porous ceramic tube. The gas is accelerated by a vacuum flow transducer (eductor) connected to the exhaust end of the porous filter tube. At the critical velocity of 88 ft./sec the vacuum on the outer surface of the filter tube removes a portion (1/20) of the gas phase from within the porous tube. Only sample gas and slight amounts of entrained mists will penetrate the filter wall. Particle build-up on the inner surface of the filter tube is inhibited by the scrubbing effect of large particles as they accelerate through the ceramic tube.



Eductor
Blowback Valve
Calibration/Purge Inlet
Extension Tube
Inertial Filter
Sample Outlet
Steam Inlet

Figure 5.49. STI Probe Configuration.

As illustrated in Figure 5.50, the gas conditioning system receives a particulate free gas stream at a constant temperature from the ceramic probe.



AIR SUPPLY
AIR PRESSURE SWITCH
PI-1
PRESSURE REGULATOR
V-3
INERTIAL FILTER PURGE
PR-1
CERAMIC PROBE
LIQUID RESERVOIR PURGE VA.
C
NO
NC
V-4
EDUCTOR
BLOWBACK VALVE
V-1
V-8
VAPORIZER FILTER
F-1
D-1
PERMEATION DRYER
VENT
SAMPLE VACUUM SWITCH
NO
V-6
C
NO
NC
C
V-7
HEAT EXCHANGER
DRAIN VALVE
V-5
VENT
STEAM SUPPLY
CALIBRATION GAS INLET

Figure 5.50. STI TRS Conditional System.

The sample gas is heated and maintained at constant temperature by the steam used to drive the ceramic filter's eductor. The high-boiling condensibles are removed by condensation and wall absorption on the helical coil condenser tube within the Pyrex heat exchanger. Figure 5.51 illustrates the double vortex coils used in the STI system.

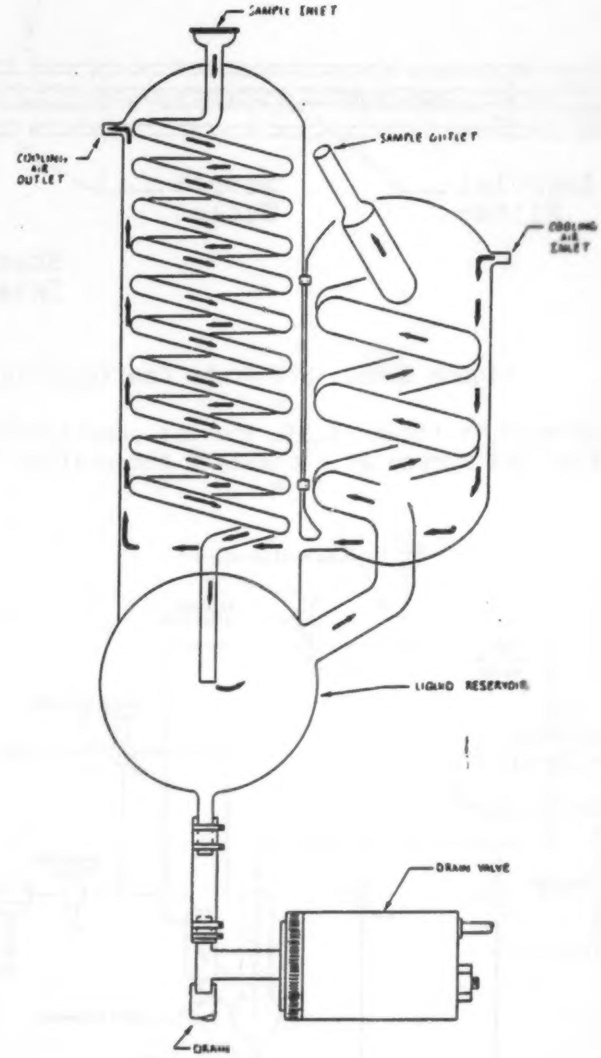

SAMPLE INLET
COOLING AIR OUTLET
SAMPLE OUTLET
COOLING AIR INLET
LIQUID RESERVOIR
DRAIN VALVE
DRAIN

Figure 5.51. STI Heat Exchanger/Condenser Assembly.

During the condensation of the high boiling condensibles, water is also condensed and is collected in the head space trap at the bottom of the condenser tube. Since the pressure in the condenser tube is lower than that of the process gas stream, the water and high boiling condensibles can be removed by the head space trap and automated drain. This method does not alter the TRS or O_2 concentration of the sample gas. From the condenser, the gas enters a filter body (vaporizer filter). The purpose of the vaporizer filter is to raise the gas temperature well above the water dew point and to act as a safety filter from the dryer and analyzer downstream. From there, the sample gas is dried in a permeation dryer (Perma Pure Products) comprising 100 selective membranes. The membranes are arranged in a tube-and-shell configuration with the sample gas in the tubes and a countercurrent flow of instrument air from the dry air assembly on the shell side. At the outlet of the dryer, the sample gas is free of acids, corrosives, and particles larger than 0.6 microns. The sample gas at this point has a dew point of approximately -40°F.

The probe/conditioning system employs steam injection for probe cleaning and incorporates a port for injection of calibration gases. The probe controller controls those functions as well as

- blowback time,
- air pressure,
- vaporizer temperature,
- enclosure temperature, and
- probe alarm closure.

From the probe/conditioning system the sample gas moves to the dilution module through unheated teflon lines.

5.3.9.2 Dilution Control Assembly -

The dilution control assembly dilutes the sample and calibration gases. The purpose of diluting the sample gas is to reduce the TRS and background SO_2 to ambient levels. At ambient levels, the SO_2 can be removed by the dry-base SO_2 scrubber. After oxidation the TRS compounds can be measured on an EPA (ambient air) reference method SO_2 detector. Sample dilution also ensures that adequate oxygen is available for the quantitative oxidization of the four TRS compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide) to sulfur dioxide.

The dilution control system incorporates precision orifice flow controllers and mass flow controllers for sample and calibration gas. The flow controller outputs are independent of down stream pressure. They require only one atmosphere (approx. 15 psig) of pressure drop across the controllers to maintain stable flow. The precision orifice controllers utilize multistage jets to accomplish the flow rate stability. The mass flow controllers operate on a variable orifice which compensates for fluctuations in mass flow rate with variations in downstream pressure. The dilution system is also the inlet for the calibration gas supplied to the probe/conditioning system during calibration.

After the pollutants in the gas stream have been diluted to ambient concentrations, SO_2 is removed by a dry bed scrubber.

5.3.9.3 Sulfur Dioxide Scrubber -

The sulfur dioxide (SO_2) scrubber is a molecular sieve based absorber. The sample gas passes directly through a canister filled with the coated sieves which selectively remove SO_2 from the gas stream. From the SO_2 scrubber the sample gas containing the TRS passes directly into the thermal oxidizer.

5.3.9.4 Thermal Oxidizer -

The thermal oxidizer (quartz furnace) is a quartz tube controlled to a temperature sufficient to convert hydrogen sulfide, methyl mercaption, dimethyl sulfide, and dimethyl disulfide to SO_2 by thermal oxidation. The oxidation occurs in the quartz tube as the sample gas (oxygen must be present) passes through. The temperature is controlled by a resistance heating coil around the quartz tube. The temperature of the coil is controlled by a variac voltage controller and displayed on a front panel mounted pyrometer. The output gas is routed to the ambient specific analyzer for SO_2 analysis, from which TRS is reported as sulfur.

5.3.9.5 Analyzer

The STI analyzer utilizes the well established principle of fluorescence spectroscopy to measure SO_2 in a gas stream.

In fluorescence spectroscopy, a pulsating ultraviolet light is focused through a narrow bandpass filter into a fluorescent chamber. The TRS as SO_2, if present, is excited to a higher energy level. However, in a very short time (10^{-9} to 10^{-8} second), the SO_2 excited molecule returns to its original state, giving off characteristic decay radiation. A second filter in front of a photomultiplier tube allows only this energy to reach the tube. The energy detected by the photomultiplier tube is directly proportional to the concentration of SO_2 in the sample stream.

Because the regulations require reporting TRS corrected to a percent oxygen, STI utilizes the Teledyne Oxygen Analyzer to monitor the oxygen content of the gas stream prior to dilution. The percent oxygen is detected by a micro fuel cell detector. The fuel cell is specific to oxygen and has a micro fuel cell detector. The fuel cell is specific to oxygen and has a linear response from 0-100%.

The oxygen and SO_2 analyzers, along with the dilution, scrubber and oxidation systems are all housed in an analyzer rack, as illustrated in Figure 5.52.

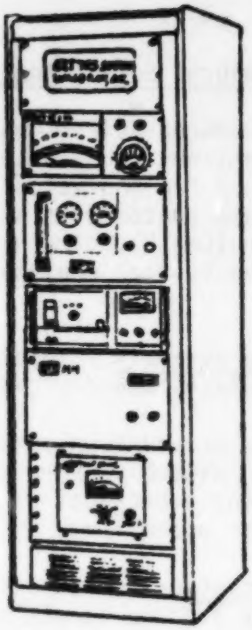


Figure 5.52. STI Analyzer Rack.

5.3.9.6 Data System -

The STI Data System functions are to log data and generate output reports. The data system incorporates the following components:

- Computer - 128 K bytes of RAM Memory (basic programming);
- Disc Drive - 5 one-fourth disc, capable of 512 K bytes of data storage;
- CRT Display;
- Battery back-up on full data system;
- Micro-Mac 4000 Input/Output system; and
- Printer - 10 inch, impact dot matrix.

All operator interface with the Data System is accomplished through special function keys on the computer keyboard.

A manual switch panel is provided to control all stream and calibration solenoid valves. These switches are normally operated in the AUTO position. This allows the data system to control the valves. The manual valve switches are required for system start up and troubleshooting.

5.3.10 Bendix Total Reduced Sulfur Analyzer

The Bendix Total Reduced Sulfur Analyzer is based upon Federal Reference Method 16- Semicontinuous Determination of Sulfur Emissions from Stationary Sources. The analytical principle is gas chromatography (GC), with flame photometric detection (FPD) of hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide, $(CH_3)_2S$ and dimethyl disulfide $(CH_3)_2S_2$. The typical analyzer system consists of five subsystems

- probe/conditioning assembly - conditions stack sample emissions and provides a particulate-free dry gas sample to the analyzer system,
- support assembly - provides pneumatic and electrical control for probe/conditioning assembly operation. The umbilical assembly transports gases and electrical signals between the probe/conditioning and support assemblies,
- sample transport system - provides analytical flow control and includes a pump as a prime sample mover. This system extracts the sample from the stack through the sample conditioning system and supplies the specified sample flow rate to the analyzer system,
- analyzer system - the analyzer is the sensor portion of the system enabling the analysis of stack emissions, and
- system control - specific functions of this system includes control of electromechanical devices (i.e. solenoids and sliding plate valves) located in the analyzer and sample conditioning system, data collection, computation, recording, and/or reporting.

Figure 5.53 illustrates the major components of the Bendix Total Reduced Sulfur Analyzer System.

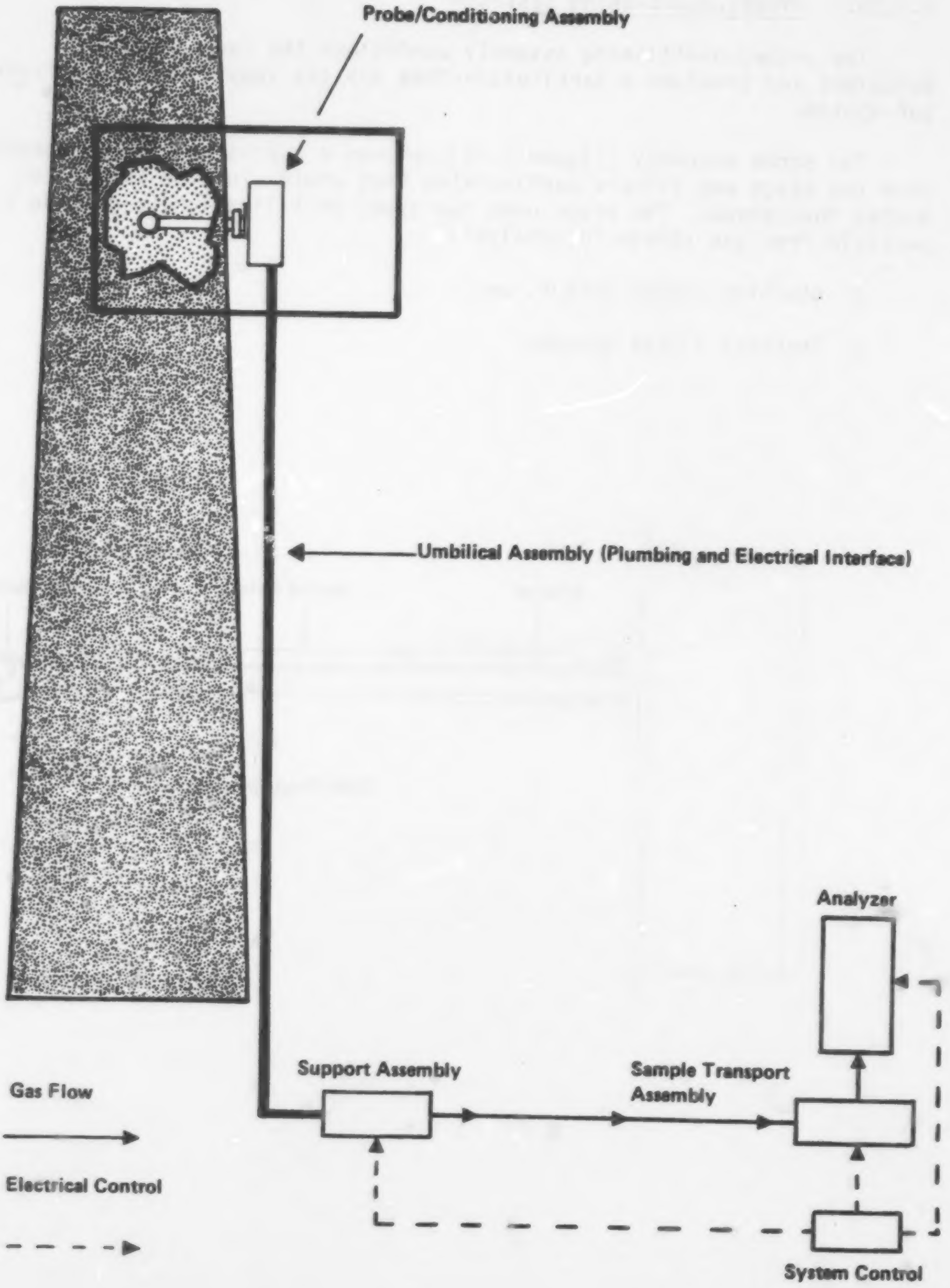

Probe/Conditioning Assembly
Umbilical Assembly (Plumbing and Electrical Interface)
Analyzer
Support Assembly
Sample Transport Assembly
Gas Flow
Electrical Control
System Control

Figure 5.53. Bendix Total Reduced Sulfur Analyzer System.

5.3.10.1 Probe/Conditioning System -

The probe/conditioning assembly conditions the sample stack emissions and provides a particulate-free dry gas sample to the analyzer sub-system.

The probe assembly (Figure 5.54) removes a representative gas sample from the stack and filters particulates that would clog the analytical system downstream. The probe uses two types of filtration to provide a particle free gas stream for analysis

- stainless steel screen, and
- inertial filter system.

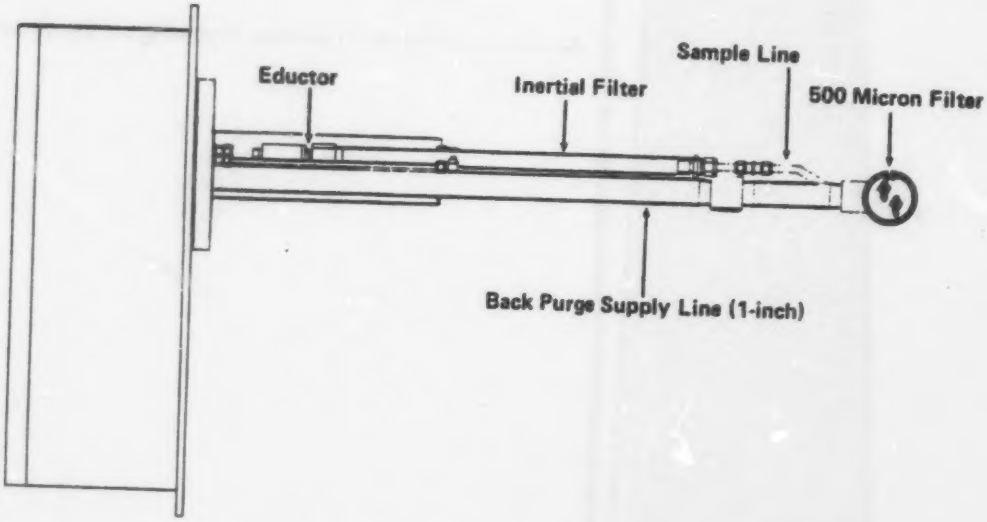

Sample Line
Eductor
Inertial Filter
500 Micron Filter
Back Purge Supply Line (1-inch)

Figure 5.54. Bendix Probe/Conditioning Assembly.

The stainless steel screen filter located at the sample inlet prevents large particles (≥500 micron) from entering the probe and secondary filtering mechanism.

The sample gas passing through the screen is drawn into the probe to the secondary inertial filtration system within the stack by an air driven eductor located on the probe. As illustrated in Figure 5.55, the inertial filter is constructed of a concentric tube of sintered stainless steel and an outer tube of stainless steel pipe.

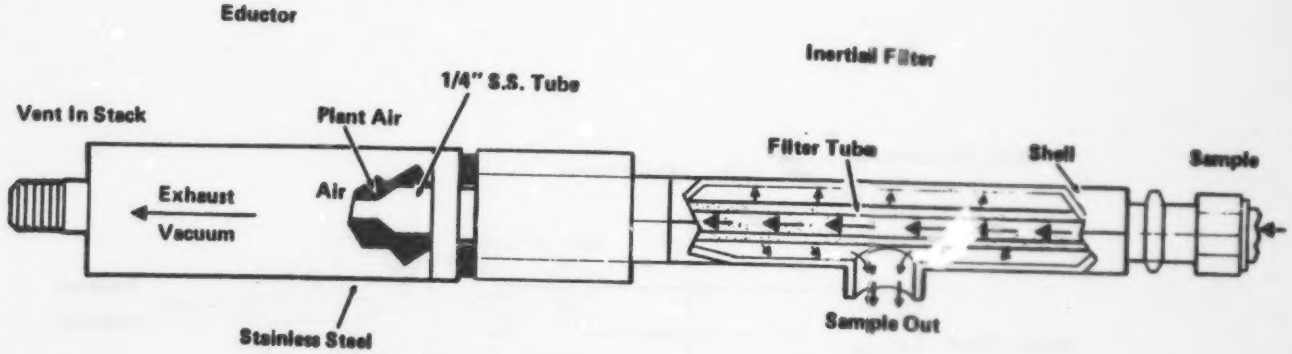

Eductor
Inertial Filter
1/4" S.S. Tube
Vent in Stack
Plant Air
Filter Tube
Shell
Sample
Exhaust
Air
Vacuum
Stainless Steel
Sample Out

Figure 5.55. Bendix Inertial Filter Assembly.

The sintered stainless steel has an effective pore size of 5 microns. In operation, stack gas is extracted through the inner tube by the eductor at a flow rate of 56 liters/minute. Downstream of the probe/conditioning assembly is a second pump which extracts gas from the porous sintered tube at a rate of 3 liters/minute. This action actually causes gas to diffuse through the inner tube to the outer tube by the downstream sampling pump. As illustrated in Figure 5.55, particulates flowing through the inner sintered tube travel at such high velocity that they are unable to make the 90° turn into the secondary gas stream. The low sampling volume to internal flow volume ratio aids in this process. Consequently, the sample gas is free of particles down to 5 microns due to the initial screen and the inertial filter mechanism.

From the sample extraction system, the stack gas sample is dried in the conditioning system, as illustrated in Figure 5-56.

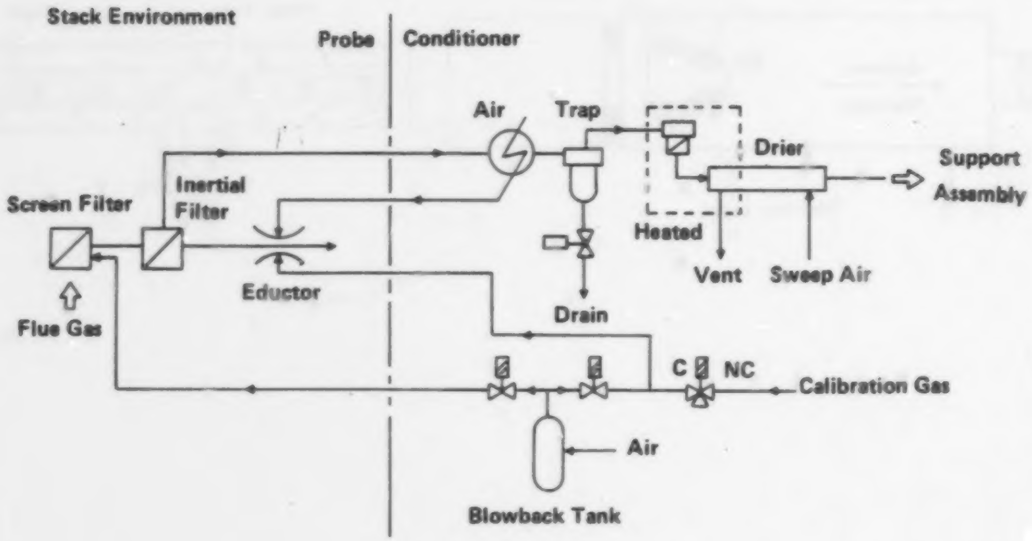

Stack Environment
Probe
Conditioner
Air
Trap
Drier
Support Assembly
Screen Filter
Inertial Filter
Heated
Eductor
Vent
Sweep Air
Flue Gas
Drain
C
NC
Calibration Gas
Air
Blowback Tank

Figure 5.56. Bendix Sample/Extraction System.

The conditioning assembly removes entrained liquids and water vapor from the sample. The sample is extracted through the inertial filter, entering the conditioning system before it is pulled through a teflon tubing air heat exchanger. The teflon tube heat exchanger utilizes air from the air supply as the cooling medium. Cooling air flow is counter to the sample flow. Any condensibles or entrained liquids are collected in a liquid trap. The stack sample is pulled from the head space of the trap (reservoir) and transported into a vaporizer located in a temperature controlled block. The vaporizer is heated to approximately 120°C. An emergency filter located within the vaporizer protects the permeation dryer from particulates during upset conditions. The vaporizer aids the permeation dryer, vaporizing any entrained liquids. The sample is then pulled through a 200 tube permeation dryer. The first 10 inches of the dryer are located in a heated enclosure for increased dryer efficiency. Water is removed from the sample gas by a unique ion transfer mechanism within the Perma Pure dryer. Purging the outer shell of the dryer with dry air transfers water vapor contained in the sample to the purge gas. This drives sample gas to a dew point of less than 11°C. Clean, dry sample gas then exits the conditioning assembly.

Figure 5.57 displays the major components of the conditioning system.

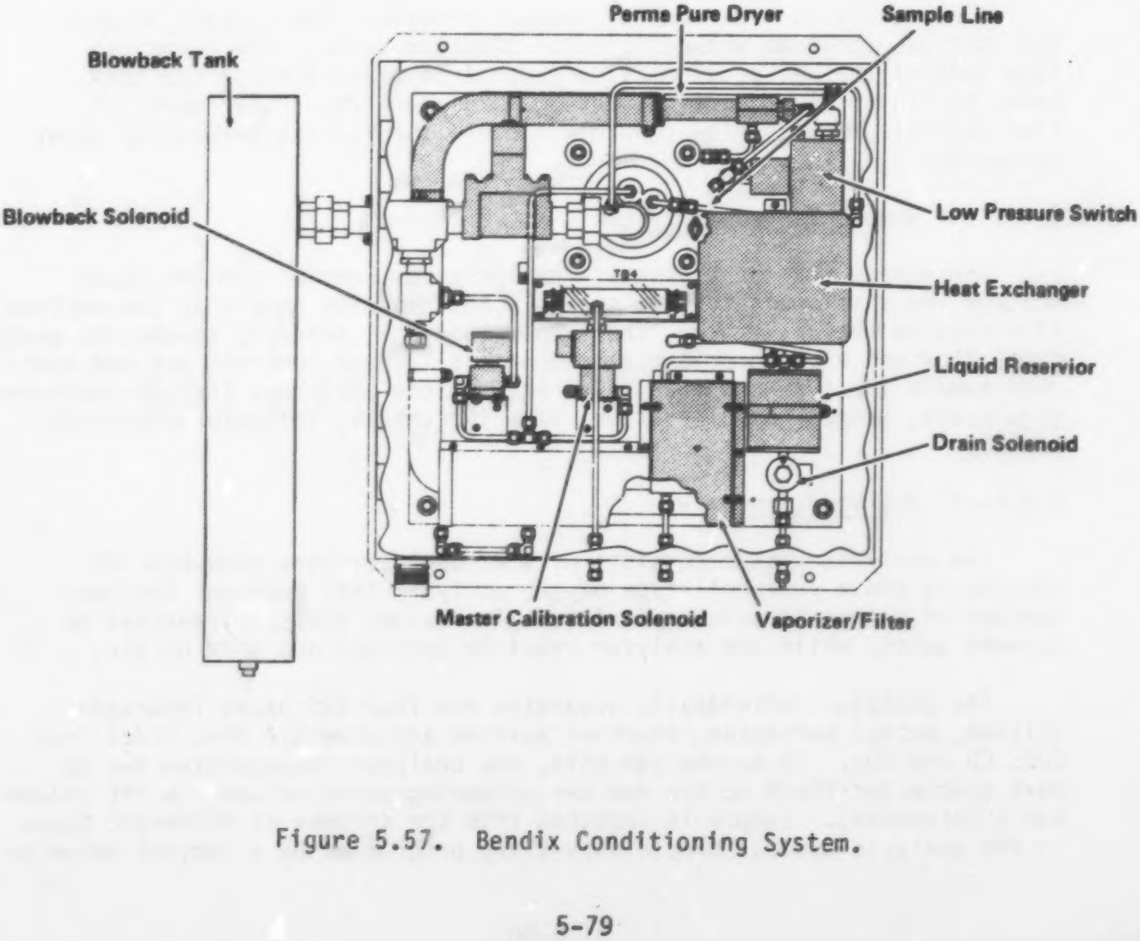

Perma Pure Dryer
Sample Line
Blowback Tank
Blowback Solenoid
Low Pressure Switch
TB4
Heat Exchanger
Liquid Reservior
Drain Solenoid
Master Calibration Solenoid
Vaporizer/Filter

Figure 5.57. Bendix Conditioning System.

Two additional functions of the probe/conditioning system are backpurge and span gas injection. At predetermined time intervals a backpurge of the 500 micron screen is accomplished with high pressure air via a pressurized air tank. Any particles embedded in the screen are blown back into the stack. This cleaning action renews the filter. After the blowback mode, the air tank is recharged for approximately 15 seconds. Then the bypass purge and drain solenoid valves are actuated for approximately 10 seconds. During this time high pressure air purges the inertial filter shell space.

During the calibration mode, calibration gas flows into the inertial filter shell space. Simultaneously the air supply to the eductor is stopped, preventing contamination of calibration gas with stack gas. Introduction of excess calibration gas to the inertial filter causes the filter to act as a manifold for referencing calibration gas to the same pressure as in the normal sampling mode. The calibration gas is then extracted by the secondary pump located downstream of the probe/conditioning system.

5.3.10.2 Support Assembly -

The support assmebly contains three flow channels which provide flow control for probe/conditioning assembly support gases.

The zero/span flow control channel provides flow control of zero and span gas input to the calibration solenoid valve. The plant air flow control channel provides flow control of plant air for the blowback, bypass purge and drain solenoid mode operation. The sweep air flow channel provides flow control of sweep air for the permeation dryer operation.

5.3.10.3 Sample Transport System -

The sample transport assembly extracts the sample from the stack through the sample conditionng assembly and supplies sample at the desired flow rate to the analyzers. The sample transport assembly houses the analytical flow and electromechanical components. These controls set and indicate sample input pressure and flow rate to the analyzers through pressure regulators, gauges, needle valves, flow indicators, solenoid valves and pumps.

5.3.10.4 Analyzer System -

The analysis system consists of a GC analyzer that measures TRS components and a fuel cell-type oxygen analyzer that measures the percentage of oxygen in stack emissions. The oxygen analyzer requires no support gases, while the analyzer requires hydrogen and carrier air.

The analyzer individually separates the four TRS gases (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) from COS, CO and CO_2. To accomplish this, the analyzer incorporates two 10 port sample backflush valves and two chromatographic columns (a PPE column and a Chromapak). Sample is injected into the columns at different times in the analysis cycle. Sample valves are programmed by a control valve to

159

route column output to the FPD when TRS component of interest is eluting. Figure 5.58 displays the analyzer rack assembly for these various components of the GC system.

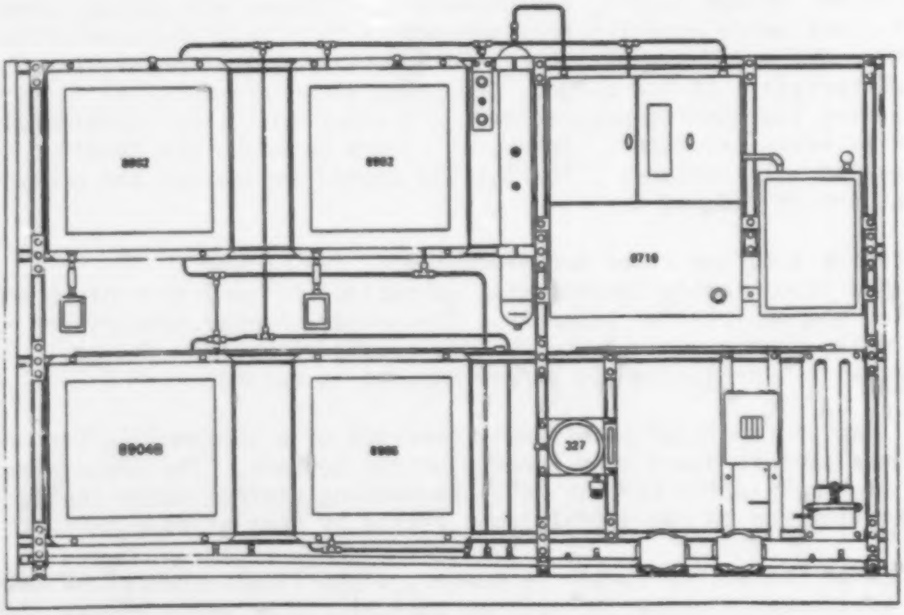

8802
8802
8710
8904B
8906
327

Figure 5.58. Bendix Analyzer Rack Assembly.

Reduced sulfur compounds are analyzed by the following mechanism. Sample gas enters the SAMPLE IN connector of the analyzer via the sample transport assembly. The sample then enters the sample loop. Carrier gas enters the instrument via the CARRIER inlet fitting and then enters the detection cell through a pressure regulator at the detector cell.

Hydrogen enters the unit from an external cylinder via the rear panel bulkhead connection. The hydrogen then flows through a series of regulators to the detector cell to sustain the flame.

Through the use of two sample loops and four columns, each venting or forcing the TRS containing gas through selected columns, the analysis of the reduced sulfur as the different species elute at different times is accomplished.

Column selection is based on sample concentration and volume, which determines the physical characteristics of the column (material of construction, column length, and diameter). Columns are coiled tubes packed with inert solid material that supports a thin film of nonvolatile liquid phase. The solid support, type and amount of liquid phase, physical characteristics of the column, and temperature are critical factors for obtaining the desired separation. All other analytical considerations such as valve selection, timing, etc., are based on the specific column selection. The columns allow for the needed separation for analytical detection of reduced

ntaining a teflon lined burner chamber. The burner chamber is optically coupled (via an optical filter) to a nitrogen sealed photomultiplier assembly. The burner chamber consists of a hydrogen well, burner, and ignitor. As a sample flows into the cell, it mixes with hydrogen at the burner tip and is burned.

The photomultiplier assembly consists of a photomultiplier tube, printed circuit board, and thermoelectric coolers. The coolers maintain the photomultiplier tube at 25°C, preventing thermal noise (background signal related to non-signal light caused by heat or dark current).

When the sulfur sample is burned, light (luminescence) is emitted. The luminescence passes through an optical filter which blocks light not of the characteristic wavelength (394 nanometers) of sulfur. The optical filter eliminates interference from non-sulfur components (i.e. hydrocarbons). The light is sensed by a photomultiplier tube which outputs current proportional to the square of sulfur concentration. The combination of gas chromatography with flame ionization detection is very sensitive to sulfur bearing species. Figure 5.59 illustrates the eluting pattern with subsequent detection by the photomultiplier tube of the reduced sulfur components of the gas stream.

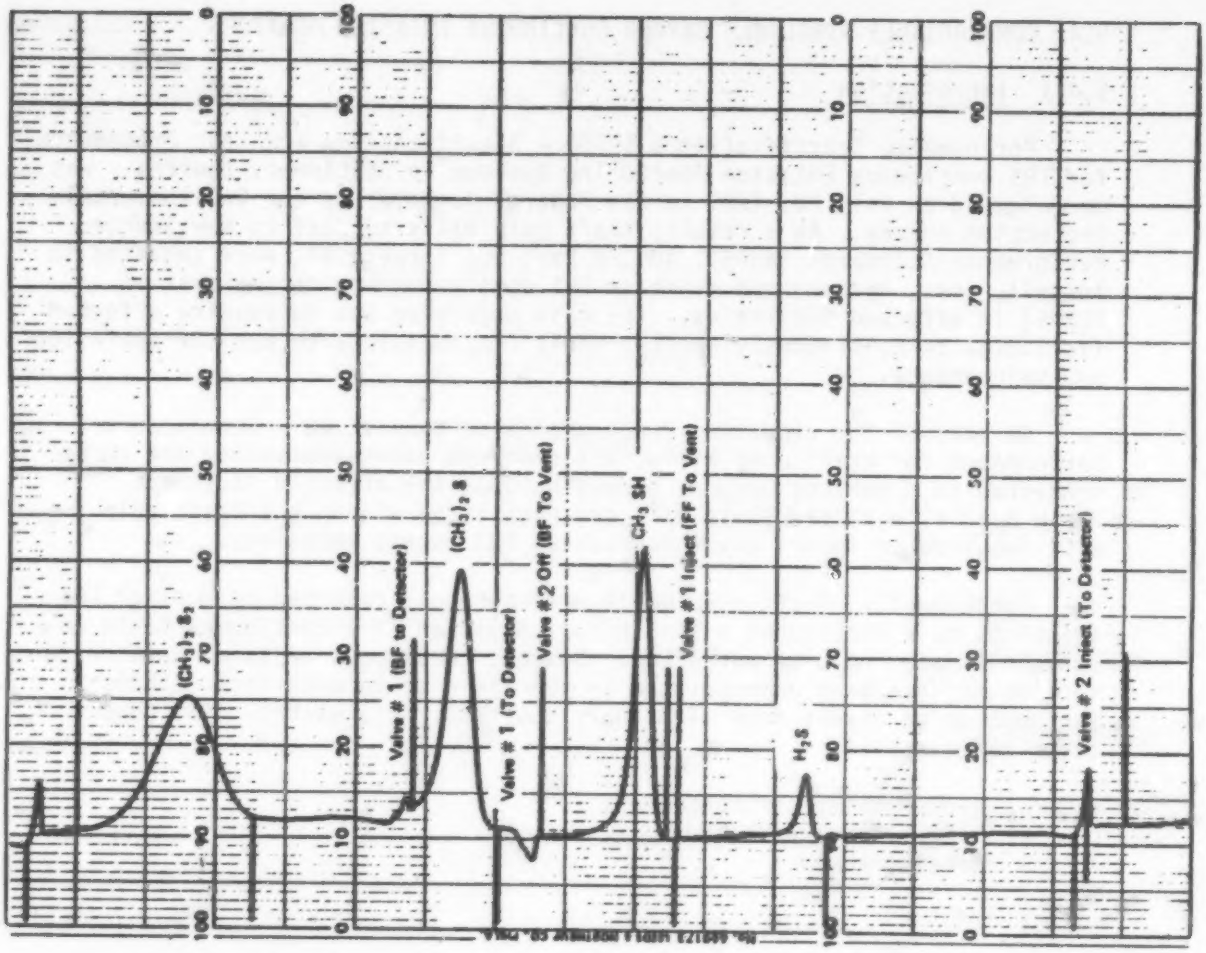


Figure 5.59. Bendix TRS Chromatogram.

5.3.10.5 System Control -

The system control contains the software packaged for generating all data to meet EPA reporting requirements. It performs all control, logic and data handling functions of the TRS system. The TRS software package supports the front panel keyboard/display, and a remote teleprinter.

Coupled with the TRS system is an oxygen analyzer for continuous measurement of oxygen. The system control receives the oxygen concentration and applies that value to the TRS measurement to develop a TRS corrected concentration.

5.4 COMMERCIALLY AVAILABLE OXYGEN CONTINUOUS EMISSION MONITORS

5.4.1 Introduction

Performance Specification 5 (PS5) - Specifications and Test Procedures for TRS Continuous Emission Monitoring Systems in Stationary Sources - was promulgated on July 20, 1983 in the Federal Register by the Environmental Protection Agency. As a result, Kraft pulp mills subject to New Source Performance Standards (NSPS), 40 CFR Part 60, Subpart BB, were required to install, test, operate and maintain TRS continuous monitoring systems (CEMS) in affected facilities. The main objective was to require affected facilities to continuously monitor their TRS emissions to monitor operation and maintenance.

As part of the reporting requirements of Subpart BB - Standards of Performance for Kraft Pulp Mills, all reported excess emissions are to be corrected to a percent oxygen, depending upon the affected facility. Table 5.12 illustrates those affected facilities within the Kraft pulp mill required to report oxygen-corrected TRS excess emissions.

Consequently, Kraft pulp mills were not only required to monitor TRS emissions on a continuous basis, but also oxygen on a continuous basis so emissions data could be corrected. Several continuous emission monitoring techinques have been demonstrated in the field to be excellent methods for monitoring oxygen from stationary sources. This section will cover three basic methods:

- Electrochemical Transducer;
- Electrocatalytic; and
- Paramagnetic.

TABLE 5.12
STANDARDS OF PERFORMANCE FOR KRAFT PULP MILLS
REGULATED EMISSIONS CORRECTED TO PERCENT OXYGEN

Source Category	Affected Facility	Pollutant	Emission Limit	Monitoring Requirement
Subpart BB - Kraft Pulp Mills Proposed/effective 9/24/76 (41 FR 42012)	Recovery furnace	Particulate	0.044 gr/dscf (0.10 g/dscm) corrected to 8% oxygen	No requirement
Promulgated 2/23/78 (43 FR 7568)		Opacity	35%	Continuous
Revised 8/7/78 (43 FR 34784)		TRS (a) straight recovery	5 ppm by volume corrected to 8% oxygen	Continuous
		(b) cross recovery	25 ppm by volume corrected to 8% oxygen	
	Smelt dissolving tank	Particulate	0.2 lb/ton (0.1 g/kg)BLS	No requirement
		TRS	0.0168 lb/ton (0.0084 g/kg)BLS	No requirement
	Lime kiln	Particulate (a) gaseous fuel	0.067 gr/dscf (0.15 g/dscm) corrected to 10% oxygen	No requirement
		(b) liquid fuel	0.13 gr/dscf (0.30 g/dscm) corrected to 10% oxygen	No requirement
		TRS	8 ppm by volume corrected to 10% oxygen	Continuous
	Digester, brown stack washer, evaporator, oxidation, or stripper systems	TRS	5 ppm by volume corrected to 10 oxygen	Continuous
			*exceptions; see standards	Effluent gas incineration temperature; scrubber liquid supply pressure and gas stream pressure loss

5.4.2 Oxygen Analytical Techniques

5.4.2.1 Electrochemical Transducer -

The most common method of detecting O_2 in a gas stream is the electrochemical transducer. The electrochemical transducer consists of a sensing membrane, electrolytic reservoir and a counter electrode all in a self contained cell. In operation, the flue gas is drawn into the electrochemical transducer, where the selective semi-permeable membrane allows only the pollutant gas to diffuse. The pollutant undergoes electrooxidation, releasing electrons. The net reaction is a release of electrons to the counter-electrode by means of the electrolytic reservoir. Figure 5.60 illustrates this movement of electrons throughout the electrochemical transducer. If the electron flow is diffusion controlled, the current will be directly proportional to the concentration of reactants. This is known as Fick's Law of Diffusion.

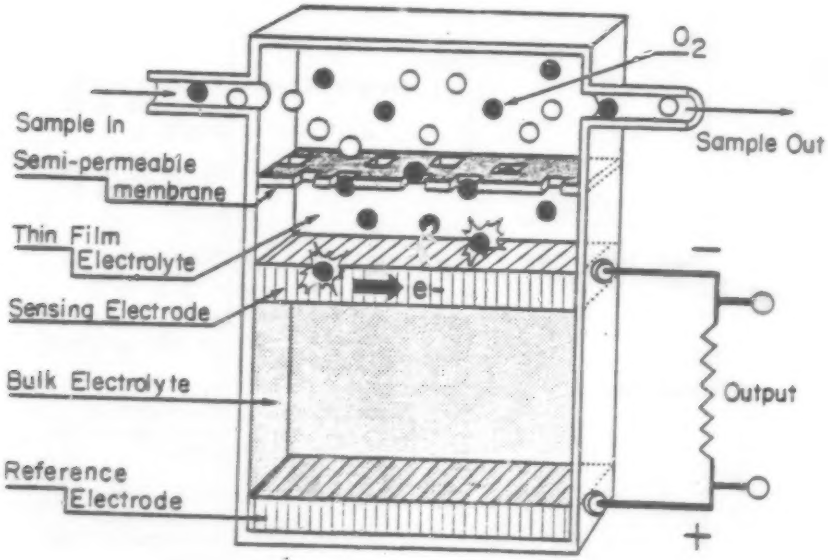

O_2
Sample In
Sample Out
Semi-permeable membrane
Thin Film Electrolyte
Sensing Electrode
e-
Bulk Electrolyte
Reference Electrode
−
Output
+

Figure 5.60 Electrochemical Transducer

Consequently, two basic techniques are used in the electrochemical transducer:

(1) utilization of a selective semipermeable membrane that allows the pollutant molecule to diffuse to an electrolytic solution; and

(2) measurement of the current change produced at an electrode by the oxidation/reduction of the dissolved gas at the electrode.

The selectivity of one pollutant diffusing through the membrane is affected by two important design features. First, the membrane is specifically selected for that pollutant of interest. Second, a retarding potential is maintained across the electrodes of the system to prevent the diffusion/oxidation of other pollutant species that are not as easily oxidized. The oxidation-reduction reaction occurs at the sensing electrode because the counterelectrode material has a higher oxidation potential than that of the species being reacted. In the cell, the sensing electrode has a potential equal to that of the counterelectrode minus the iR drop across the resister. The sensing electrode is electrocatalytic in nature and, being at a high oxidation potential, will cause the oxidation of the pollutant and a consequent release of electrons. Other pollutant molecules, having higher or lower oxidizing potential, therefore cannot participate in the cell reaction. The system therefore becomes selective by design.

Overall, the detection of the pollutant gas is achieved by the following mechanism: (a) the diffusion of the pollutant gas through the semi-permeable membrane; (b) the dissolving of the gas molecules in the thin liquid film; (c) the diffusion of the gas through the thin liquid film to the sensing electrode; (d) oxidation-reduction at the electrode; (e) transfer of the charge to the counterelectrode; and (f) reaction at the counterelectrode. The electron current through the resistor can then be picked off as a voltage and suitably monitored.

The electrochemical transducer comes in a number of configurations, depending upon the manufacturer: Various claims have been made about the response and selectivity of the instrument related to the cell design. The advantages of these systems are in their small size and portability. Compared to practically all other source monitoring instruments, they are the least expensive. These two factors make them ideal for spot checks during a source inspection or as warning detectors. Each sensor is a sealed unit. The sensor operating life may vary from 3 to 12 months, depending upon the condition of the sample entering the cell. Particulate and high temperature shorten the life of the detector cell. Removal of particulate and lowering sample temperature will lengthen the life of the cell.

In operation, a gas sample is extracted through a filtered probe to a condenser by way of a pump. After particulate and moisture removal, the sample is "pushed" through the analyzer at a flow rate of 0.5 to 2.0 scfh. The instrument reading is relatively independent of flow rate. However, the sensor is designed for operation at atmospheric pressure. It can be operated at pressures slightly above or below atmospheric, but any pressure changes should occur slowly in order to prevent damage to the sensor. The instrument operates best under positive pressure since the zero/span gases are supplied under pressure.

5.4.2.2 Electrocatalytic Technique -

In recent years, a new method of monitoring oxygen in a sample gas stream has developed from the fuel cell technology. Similar to the electrochemical transducer, the fuel cell replaces the bulky liquid electrolyte with a special solid catalytic electrolyte. Based on electrochemical principles, the detection of oxygen involves the movement of reference oxygen through a temperature-controlled solid porous electrolyte to the sample oxygen, based upon differential partial pressures. The closed end tube sensor, which is responsive to these changes in partial pressure, is coated on the inside and outside with platinum and maintained at a temperature of 1550°F. At this temperature, vacancies in the lattice structure exist. These vacancies provide a path for the oxygen ion to migrate from one side of the electrolyte to the other due to existence of the differential pressure on either side of the electrolyte. The migration of oxygen from the reference side to the sample side produces a current through a basic oxidation/reduction reaction. A schematic of a typical electrocatalytic sensing system is shown in Figure 5.61.

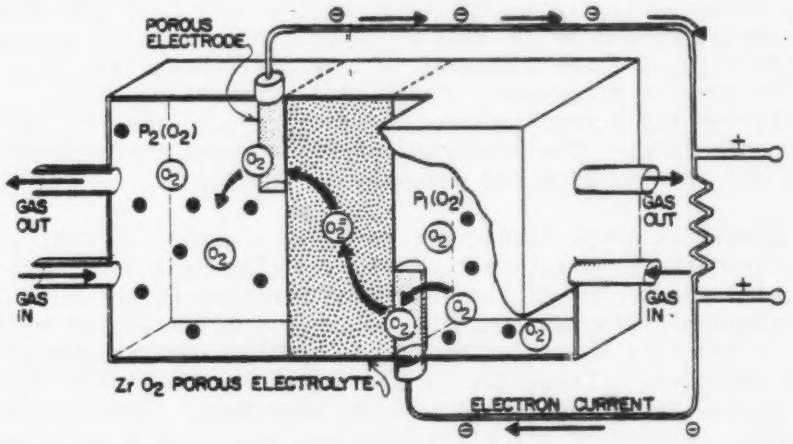


Figure 5.61 Electrocatalytic Technique

In sampling combustion gases, the partial pressure of the oxygen in the sample side will be lower than the partial pressure of oxygen in the reference side. This imbalance of pressures causes the oxygen on the reference side (high partial pressure) to pass through the heated porous electrolyte to the sample side (low partial pressure) in an attempt to equilibrate the two sides. At the cathode, the reference gas , which is generally ambient air (20.9% O_2), is electrochemically reduced by the following equation:

$$O_2 + 4_e^- \longrightarrow 2O^=$$

[The electrons (e^-) are supplied to the cathode by a load in the circuit.]

The oxygen ion, $O^=$, becoming part of the 1550°F zirconium electrolyte, migrates to the anode and reacts with hydrogen by the following equation:

$$2O^= + 2H_2 \longrightarrow 2H_2O + 4_e^-$$

The water produced is carried away by the sample gas. The released electrons flow through the load and back to the cathode. The electromotive force (EMF) produced from the electrochemical reactions at the cathode and anode is directly proportional to the differential partial pressures existing between the reference side and sample side of the electrolyte. This process can be represented by the Nernst equation.

$$\text{EMF} = \frac{RT}{4F} \ln \frac{P \text{ ref } (O_2\ )}{P \text{ sample } (O_2\ )} + C$$

where:

EMF = Electromotive force, volts;

R = Ideal gas constant;

T = Temperature of cell;

F = Faraday's constant;

P ref (O_2)= Partial pressure of oxygen in reference gas;

P sample (O_2)= Partial pressure of oxygen in sample gas; and

C = The cell constant.

If the cell temperature can be stabilized (1550°F) and the partial pressure in the reference gas is known, then the partial pressure in the sample gas can be calculated by the above equation.

A number of manufacturers are presently marketing oxygen analyzers. Both extractive and in-situ-type systems have been developed, providing the source operator with versatility in application. It should be noted that a constant supply of clean dry air for the reference side of the cell is required. Calibration gases can be injected into the measuring cavity contained within the ceramic thimble to check the instrument operation.

5.4.2.3 Paramagnetic Technique -

One of the earlier principles of monitoring oxygen was the paramagnetic analyzer, based upon the natural paramagnetic behavior of oxygen molecules. Molecules react differently to magnetic field. Those that are repelled are termed "diamagnetic" molecule while those that are attracted by a magnetic field are termed "paramagnetic". Diamagnetic molecules have paired electrons: the same number of electrons spinning counterclockwise as spinning clockwise. Oxygen, however, has two "unpaired" electrons that spin in the same direction. These two electrons give the oxygen molecule a permanent magnetic moment. When an oxygen molecule is placed near a magnetic field, the molecule is drawn to the field and the magnetic moments of the electrons become aligned with it. This striking phenomenon was first discovered by Faraday and forms the basis of the paramagnetic method for measuring oxygen concentrations. There are two techniques presently marketed utilizing the paramagnetic properties of oxygen:

- Magneto-Dynamic Techniques; and
- Magnetic Wind Technique.

5.4.2.3.1 Magneto - Dynamic Technique -

The magneto -dynamic technique utilizes the paramagnetic nature of oxygen in suspending a specially construction torsion balance, as shown in Figure 5.62.

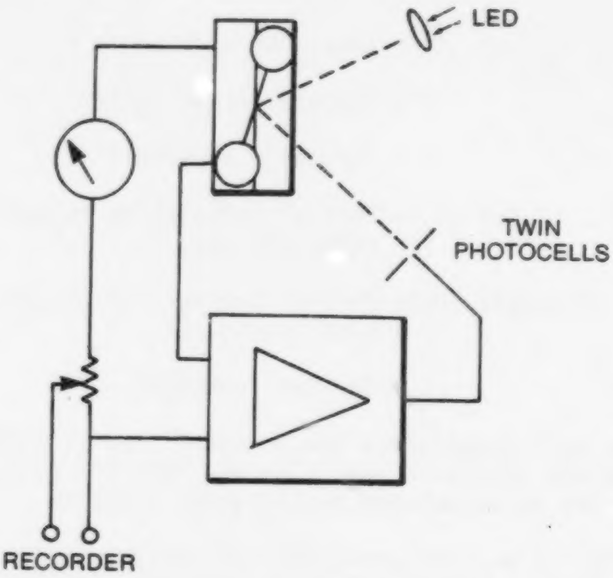


Figure 5.62. Magneto - Dynamic Technique

In operation, a diamagnetic quartz "dumb-bell" is suspended in a symmetrical, nonuniform magnetic field within the instrument. A mirror is attached to this quartz "dumb-bell" with the entire apparatus fixed upon a torsion spring. The magnetic field acts upon the diamagnetic quartz "dumb-bell" to force it to a position away from the most intense part of the field. At zero position a light source is reflected by the mirror from the suspended quartz spheres to a photocell which generates a signal used to keep a known torque applied to the torsion spring. The presence of oxygen in the sample cell changes the shape of the magnetic field causing the quartz "dumb-bell" to be further deflected. The photocell signal is used to apply a restoring torque to the spring and return the quartz spheres to the original position. The torque applied to restore the quartz to a "null balance" is proportional to the oxygen concentration present.

5.4.2.3.2 Magnetic Wind Technique -

The magnetic wind instruments are based on the fact that the paramagnetic attraction of the oxygen molecule decreases as the temperature increases. A typical analyzer utilizes a cross-tube wound with filament wire heated to 200°C, as shown in Figure 5.63.

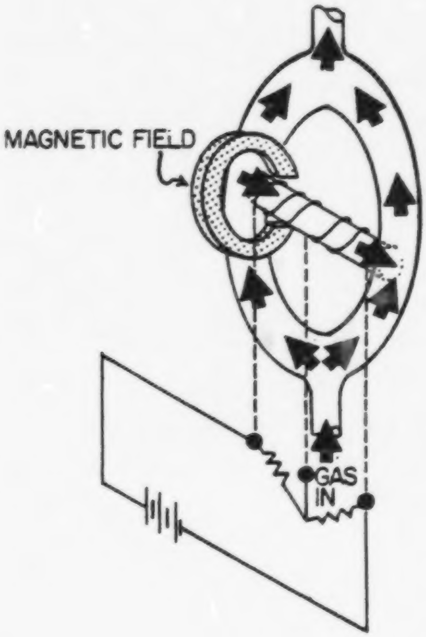


Figure 5.63. Magnetic Wind Technique

A strong magnetic field covers one half of the coil. Oxygen contained in the sample gas will be attracted to the applied field and enter the cross-tube. The oxygen then heats up and its paramagnetic susceptibility is reduced. This heated oxygen will then be pushed out by the colder gas just entering the cross-tube. A "wind" or flow of gas will therefore continuously pass through the cross-tube. This gas will, however, effectively cool the heated filament coil and change its resistance. The change in resistance detected in the Wheatstone bridge circuit can be related to the oxygen concentration.

6.0 GENERATION OF STANDARD TEST ATMOSPHERES

6.1 INTRODUCTION

As we develop new and improved techniques to monitor total reduced sulfur species from Kraft pulp mills, it has become imperative for the analytical systems to be calibrated so their results can be used as part of an agency's enforcement options. Consequently, in recent years more emphasis is being placed on the calibration of air pollution monitors. This ensures that the data generated actually represents the pollutant concentration being monitored.

Sampling systems may be designed to operate within a specific range of conditions, but due to deterioration, electrical or mechanical, the data generated by the monitor may differ from the true concentration of pollutant in the stack gas. In order to continually evaluate the performance of the sampling equipment, a known concentration of the pollutant should be challenged to the monitor. The response of the monitor to the known is compared to determine accuracy of the system. A relationship is developed between the known vs. monitor response. From this relationship, the data generated can be corrected, accounting for monitor deterioration, etc.

The methods available for generating known concentrations of reduced sulfur compounds are divided into two broad categories:

- dynamic calibration systems; and
- static systems.

In discussing these two techniques for generating known concentrations of test atmospheres, we will have to keep in mind that we are interested in part per million concentration ranges for the monitored pollutants. Attempts to prepare static standards in fixed volume containers and in bags may be impossible. Such features as adsorption, absorption, stability and other concerns must be considered. Dynamic calibrations overcome many of the inherent problems of static systems. But dynamic calibrations are not without their drawbacks. Traceability, stability, availability of standards, etc. are just some of the limitations associated with dynamic calibrations. The purpose of this section is to discuss the methods available for generating known standards of reduced sulfur compounds for both static and dynamic systems.

6.2 DYNAMIC CALIBRATION SYSTEMS

6.2.1 Permeation Tubes

In 1966, O'Keefe and Ortman, of the U.S. Environmental Protection Agency, discovered that a gas confined above its liquified form will permeate through a permeable material at a constant rate if held at a constant temperature. This discovery satisfied the primary objective of a calibration system: to generate a known concentration over a period of time. With this in mind, O'Keefe and Ortman discovered that Teflon® or other plastic materials allowed the permeation of gas through their surfaces enabling them to generate test atmospheres. By placing the liquified pollutant in a tube of Teflon® or other plastic material, sealing both ends and putting it in a water bath at a constant temperature, they discovered that they could generate known test atmospheres. This discovery led to the development of two major permeation devices:

- Permeation tubes or diffusion tubes; and
- Permeation vials.

6.2.1.1 Permeation Tube Construction -

The performance of a permeation device depends on the type of polymer film used in its construction and the pollutant. Major factors to consider in the use of a permeation device are:

- temperature;
- humidity;
- gas stability; and
- equilibrium time.

Table 6.1 lists some of the materials used to construct permeation devices and Table 6.2 lists permeation rates for a number of compounds through Teflon® film.

TABLE 6.1
PERMEATION TUBE CONSTRUCTION

Material	Trade Name	Thickness (in.)
Fluorinated ethylene propylene resin	FEP Teflon®	0.030
Fluorinated ethylene propylene resin	FEP Teflon®	0.12
Fluorinated ethylene propylene resin	FEP Teflon®	0.001
Polyethylene	-	0.027 to 0.526
Polyethylene	Alathon	0.025
Polyethylene	-	0.001 to 0.037
Polyvinyl acetate	-	0.135 to 1.332
Polyvinylidene chloride	Saran Wrap	0.025
Polyamide	Nylon 6	0.113
Polyester	Mylar	0.031
Polyethylene terephthalate	Mylar	0.00031 to 0.006
Polyethene	Diothene	0.0635 to 0.0254

TABLE 6.2
PERMEATION RATE FOR SELECTED COMPOUNDS THROUGH TEFLON FILM

Compound	Film Thickness (in.)	Temperature (°C)	Permeation Rate (ng/cm/min)
SO_2	0.012	20 + 0.5	213
SO_2	0.030	20 + 0.5	138
	0.012	20.1	203
	0.120	29.1	396
NO_2	0.012	13.8	605
	0.012	21.1	1110
	0.012	29.1	2290
Propane	0.012	21.1	53
	0.012	29.1	119
Butane	0.012	15.5	6.4
	0.012	29.1	22.3
CHF_2Cl	0.012	20	2.8
$CF^3CHClBr$	0.016	93	1.3
CH_3CHCH_3	0.030	31	0.29
$n\text{-}C_5H_{12}$	0.016	93	0.065
$C_6H_5CH_3$	0.030	20	0.00006
H_2S	0.012	35	816
CH_3SH	0.012	35	541
$(CH_3)_2SH$	0.012	35	120
$(CH_3)_2S_2$	0.012	35	12.7

The permeation tube is made by sealing a liquid chemical in a tube made of some permeable material. It is essential that the chemical be in the liquid state for the permeation tube to operate properly. In many cases the chemical is a gas at atmospheric pressure, but is maintained in the liquid state under its own saturation vapor pressure in the permeation tube. The tube is sealed at both ends with a non-permeable plug, as illustrated in Figure 6.1.

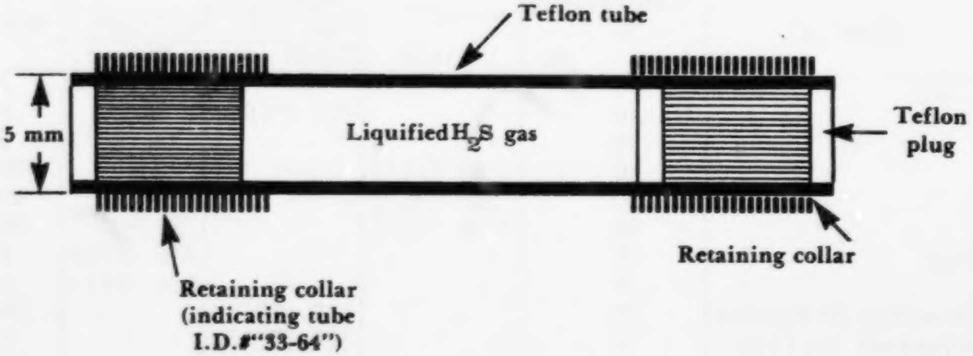


Figure 6.1. Construction of a Typical Permeation Tube

Permeation of the pollutant vapor within the tube occurs through the exposed sidewalls because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated. If the tube is held at a constant temperature, the permeation rate will remain constant. By measuring the weight loss at this constant temperature over a given period of time, the permeation rate may be determined. The output rate of the tube will remain essentially constant until nearly all of the liquid in the tube has permeated through the walls. In general, permeation tubes can be used to generate known pollutant concentration between 0.1 and 10 ppm.

6.2.1.1.1 FEP Teflon® Permeation Tubes -

FEP tubes were the first tubes developed and proved to be most practical in terms of obtaining low permeation rates. One major drawback, however, is their sensitivity to fluctuations in temperature, thus changing their permeation rate. An error of approximately 10% per °C change has been documented. Consequently, the correct temperature must be maintained when using FEP Teflon® permeation tubes.

6.2.1.1.2 TFE Teflon® Permeation Tubes -

TFE Teflon® Permeation tubes were developed and studied in recent years to provide a device with a considerably higher permeation rate. TFE permeation rates are typically 3 to 5 times higher than FEP permeation rates. Because of the higher rates available with TFE, standards can be made with materials which would normally have vapor pressures too low for the FEP devices. Similar to the FEP permeation devices, TFE Teflon® permeation tubes are also sensitive to temperature variation (± 10% per °C change).

Table 6.3 demonstrates the difference in permeation rates for both FEP and TFE Teflon® permeation tubes and permeation vials for selected chemicals.

TABLE 6.3
PERMEATION RATES FOR FEP AND TFE TEFLON® PERMEATION TUBES

Chemical	Bath Temperature, °C	Permeation Rate (ng/min/cm)			Life, Months
			Tube Wall Thickness		
		Vial[1]	0.030 in.	0.062 in.	
SO_2	30		-	265 (FEP)	7.9
	30		730 (FEP)	-	6.6
	35		-	420 (FEP)	5.0
	30	50 (FEP)	-	-	480
	30	300 (FEP)	-	-	89
	30	1300 (FEP)	-	-	20
H_2S	30		-	240 (FEP)	6
	35		-	330 (FEP)	4.4
Dimethyl Disulfide	70		130 (TFE)		28
Dimethyl Sulfide	70		300 (FEP)	-	9.5
	30		70 (TFE)	-	41
Methyl Mercaptan	30		65 (FEP)	-	46.7
	30		270 (TFE)	-	11.2

[1] Permeation rates differ for FEP vials at the same temperature due to the thickness of the vial cap.

6.2.1.2 Permeation Tube Rate -

Before a permeation device can be used in the laboratory or in the field, its permeation rate must be determined. The permeation rate, R, is determined gravimetrically. In essence, the tube is weighed, then placed in a temperature bath (±1°C) for a period of time. The tube is removed and reweighed. This process is repeated over several days to calculate a permeation rate at that specific temperature. The difference between initial and recorded weight (ng), divided by time (min.) determines the permeation rate.

$$R = \frac{(W)}{T}$$

where:

R = permeation rate, ng/min
W = weight change, ng
T = time, minutes

The permeation rate can be calculated either manually, as shown in the above equation, or recorded automatically. Figure 6.2 illustrates the apparatus used to determine the permeation rate of a permeation device automatically. Figure 6.3 displays the stripchart read-out of the automated system.

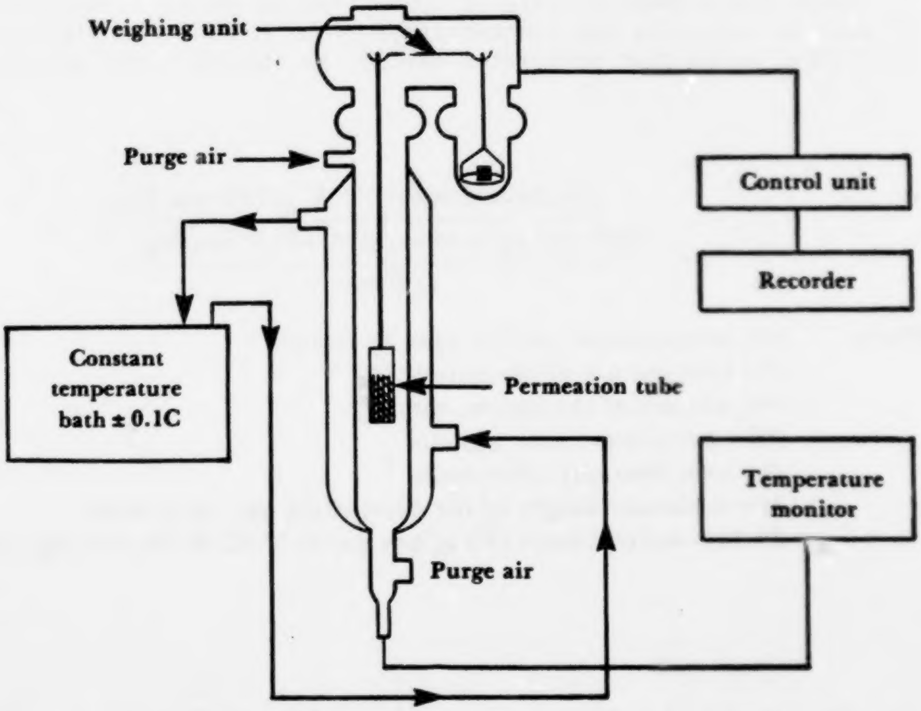

Weighing unit
Purge air
Control unit
Recorder
Constant temperature bath ± 0.1C
Permeation tube
Temperature monitor
Purge air

Figure 6.2. Automated Weighing Unit to Determine Weight Loss of a Permeation Tube

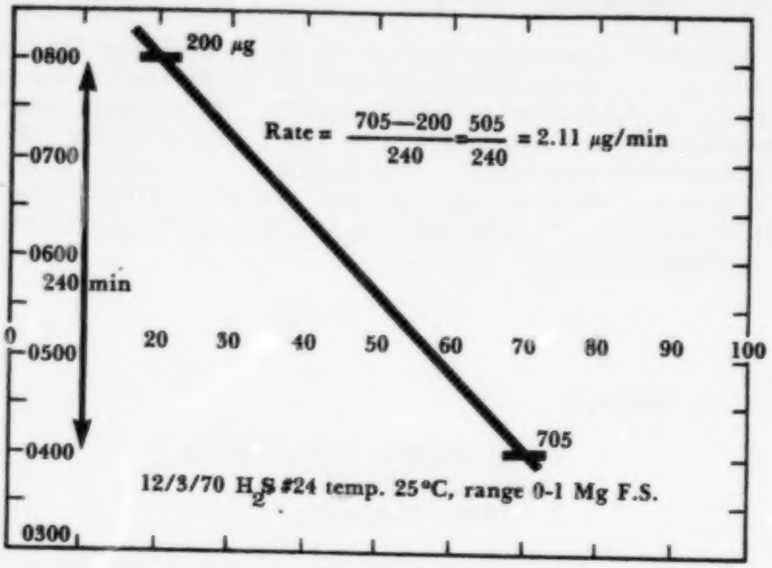


Figure 6.3. Stripchart Readout of Automated Weighing Unit for Permeation Rates

Once the permeation rate of the diffusion device is determined, it is used to calculate the concentration of pollutant test atmosphere generated, using that permeation device, by the following equation:

$$c = \frac{(PR)\left(\frac{24.46\mu\ell/\mu\text{-mole}}{(M)\ \mu g/\mu\text{-mole}}\right)\left(\frac{T\,^\circ K}{298\,^\circ K}\right)\left(\frac{760\text{ mm Hg}}{P\text{ mm Hg}}\right)}{Q\ \ell/\text{min}}$$

Where: *c = concentration, μℓ/ℓ or ppm by volume*
T = temperature of the system, °K
P = pressure of the system, mm Hg
PR = permeation rate, μg/min
Q = total flow rate, liters/min
M = molecular weight of the permeating gas, μg/μ-mole
24.46 *= molar volume ($\bar{V}$) of any gas at 25°C @ 760 mm Hg, μℓ/μ-mole*

An example of a typical permeation calibration system used in generating a known concentration of pollutant is shown in Figure 6.4. (Several tubes can be placed in temperature controlled containers to generate different pollutants at one time.)

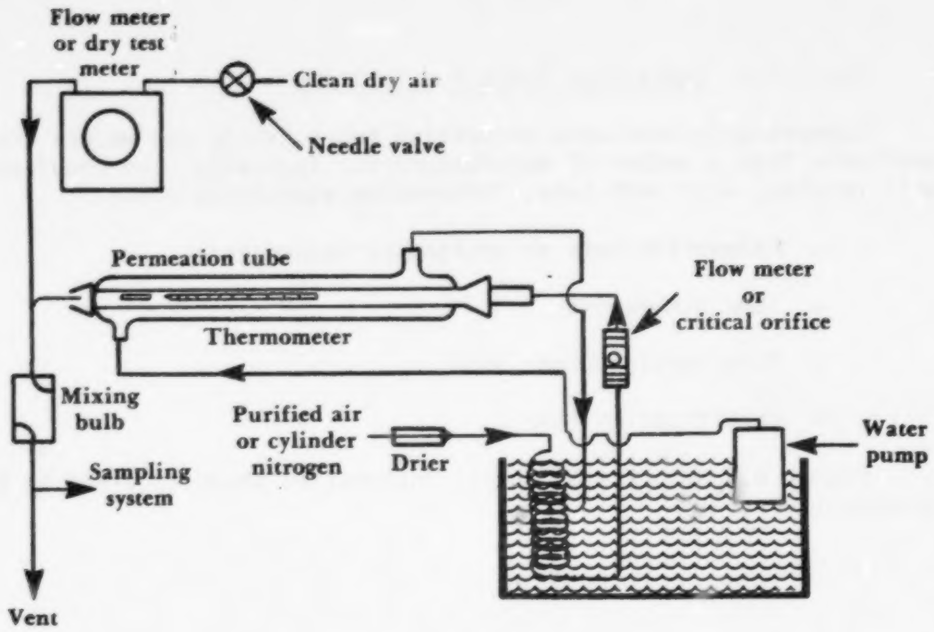

Flow meter or dry test meter
Clean dry air
Needle valve
Permeation tube
Flow meter or critical orifice
Thermometer
Mixing bulb
Purified air or cylinder nitrogen
Drier
Water pump
Sampling system
Vent

Figure 6.4. Typical Permeation Calibration System

6.2.1.3 Permeation Tube Availability

6.2.1.3.1 National Bureau of Standards - Standard Reference Materials (NBS-SRMs)

The National Bureau of Standards presently provides three Standard Reference Materials involving permeation tubes for sulfur dioxide. The tubes are available in three lengths - 2, 5 and 10 centimeters. The permeation rates are certified over the temperature range of 20 to 30°C. Table 6.4 provides a guide to the availability of NBS-SRM permeation tubes for sulfur dioxide.

TABLE 6.4
AVAILABILITY OF NBS-SRM's for SO_2

SRM #	Type	Tube Length, Cm	Permeation* Rate (µg/min)	Typical Concentrations for Various Flow Rates (ppm)		
				1 l/min	5 l/min	10 l/min
1625	Sulfur Dioxide Permeation Tube	10	2.8	1.07	0.214	0.107
1626	Sulfur Dioxide Permeation Tube	5	1.4	0.535	0.107	0.0535
1627	Sulfur Dioxide Permeation Tube	2	0.56	0.214	0.0428	0.0214

*Permeation Temperature = 25°C

6.2.1.3.2 Commercial Tubes Availability

Commercially available permeation tubes, vials and wafers are available from a number of manufacturers. Typically, the manufacturer will provide, with each tube, information associated with:

- Permeation rate at designated temperature;
- Tube dimensions;
- Tube construction; and
- Certification level

Figure 6.5 displays a typical information sheet provided by major manufacturers.

MATERIAL IN DEVICE	DEVICE TYPE*	TUBE CONSTRUCTION	WALL SIZE OR VIAL (V)	EFFECTIVE LENGTH	TEMPERATURE	PERMEATION RATE
CHEMICAL	C B CS	FEP TFE NYL	.062 .030 V	2-10 cm. 0,1-5 cm. (V)	30-70°C	ng/min

EXAMPLES:

Ammonia	CS	FEP	.062	5	30	1100
Chlorine	CS	FEP	V	0	30	320
Acrolein	B	TFE	.030	10	30	1640
Methyl Hydrazine	C	TFE	.030	6	70	1190

*C = Certified Permeation Tube
B = Batch Permeation Tube
CS = Certified Stock Permeation Devices

Figure 6.5. Permeation Tube Information

The selection of the proper permeation tube from a manufacturer can be performed in four steps.

Step 1: Identify gas of interest

Step 2: Select the gas concentration (in parts per million by volume) you need. Designate this concentration C.

Step 3: Determine minimum flow rate (in cubic centimeters/minute) needed to support the TRS continuous emission monitor. Designate this flow rate E.

Step 4: Calculate the needed permeation rate (in nanograms/min) using the following formula:

$$P = \frac{FC}{K_m}$$

Where:

P = permeation rate, ng/min;
F = flow rate, cc/min;
C = concentration, ppm by volume; and
K_m= the molar constant;

$$K_m = \frac{24.46}{MW}$$

Where: 24.46 = molar volume in liters at 25°C and 760mm Hg; and
MW = molecular weight of pollutant.

Step 5: Check the manufacturer literature to obtain closest permeation rate.

There are several manufacturers which supply certified permeation devices. Table 6.5 lists those manufacturers and their addresses.

TABLE 6.5
SUPPLIERS OF CERTIFIED PERMEATION DEVICES

Manufacturer	Address	Pollutant				
		Hydrogen Sulfide H_2S	Methyl Mercaptan CH_3SH	Dimethyl Sulfide $(CH_3)_2S$	Dimethyl Disulfide $(CH_3)_2S_2$	Sulfur Dioxide SO_2
Kin-Tek Laboratories, Inc.	Drawer J Texas City, Tx. 77590 (409)945-4529	x	x	x	x	x
Viti Metronics	2991 Corvin Drive Santa Clara, Ca. 95051 (408) 737-0550	x	x	x	x	x
Ecology Board, Inc.	9257 Independence Ave., Chatsworth, Ca. 91311 (213) 882-6795	x	x	x	x	x
Tracor, Inc.	6500 Tracor Land Austin, Tx. (512) 926-2800	x	x	x	x	x
Analytical Instrument Development, Inc.	Rt. 41& Newark St. Avondale, PA. 19311 (215) 268-3181	x	x	x	x	x
Metronics Associates, Inc.	3201 Porter Drive Stanford Industrial Park, Palo Alto, CA. 94304 (415) 493-5632	x	x	x	x	x
National Bureau of Standards	Office of Standard Reference Material US Dept. of Commerce, Gaithersburg, MD. (301)921-2045	-	-	-	-	x

6.2.1.4 Other Permeation Devices: Vials -

Permeation vials were developed to meet two specific needs. The first was to provide a device that is a low permeator. The second was to provide a larger reservoir containing the liquified pollutant to enable a longer life.

The construction of the permeation vial is very simple. As shown in Figure 6.6, the device is simply a pyrex glass container with a FEP Teflon® plug.

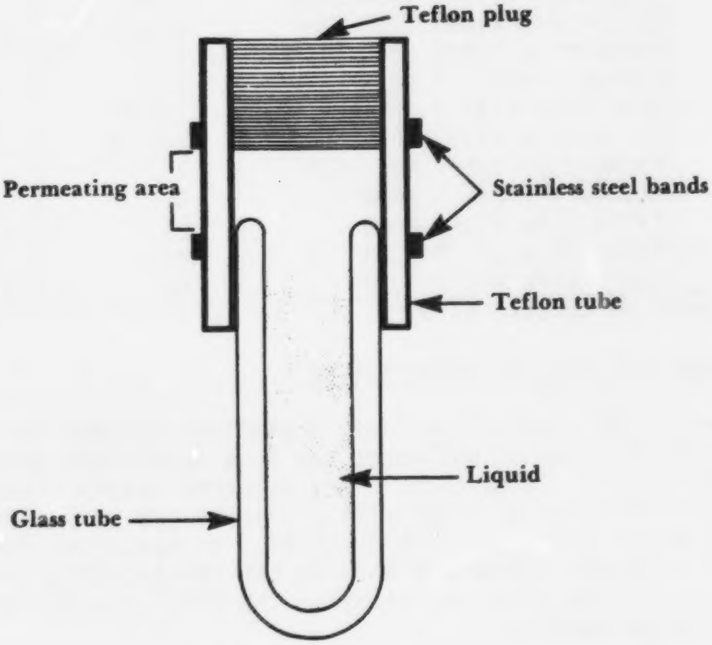


Figure 6.6. Construction of a Permeation Vial

The liquified pollutant is added to the vial and capped with the Teflon® plug. As can be seen from the illustration, the only source for the vapor to permeate is through the plug. Because the plug has a very low permeation area, the result is a reduced amount of permeating pollutant. This, coupled with a very large reservoir of liquid, enables the vial to last longer than the permeation tubes discussed earlier.

For those pollutants with a high vapor pressure, the permeation vial enables a method for generating a known concentration over a longer period of time. This is particularly true for chlorine and carbonyl sulfide. Table 6.6 lists those pollutants commercially available in permeating vials. (Those pollutants not listed in the Table can be specially ordered from the manufacturer).

TABLE 6.6
COMMERCIALLY AVAILABLE PERMEATION VIALS

Material	Device	Rate (ng/min)	Life (Months)	Width x Length (cm)
Cl_2	Standard Vials	320	72	.6 x 7
	High Rate Vial	1500-7000	14-3	.6 x 8 to 12
	Extra Life Vial	1500-7000	40-9	1 x 8 to 12
	Permeation Tube	300	1	.6 x 4 to 12
NO_2	Standard Vial	300	91	.6 x 7
	High Rate Vial	1200-5800	22-5	.6 x 8 to 12
	Extra Life Vial	1200-5800	60-13	1 x 8 to 12
	Permeation Tube	2500-11,000	1.2	.6 x 4 to 12
SO_2	Standard Vial	50	480	.6 x 7
	High Rate Vial	300-1300	89-20	.6 x 8 to 12
	Extra Life Vial	300-1300	240-56	1 x 18 to 12
	Permeation Tube	600-2600	7	.6 x 4 to 12
COS	Standard Vial	2600	8.7	.6 x 7
	Extra Life Vial	2600	24	1 x 7
Freon 12	Standard Vial	1000	24	.6 x 7
	Extra Life Vial	1000	66	1 x 7

*All rates calculated at 30°C.

6.2.2 Gas Cylinder Dilution System

One of the simplest and most economical systems for providing a known concentration of pollutant gas to a monitoring system is a gas dilution system. In essence, a gas dilution system involves mixing a known concentration of a gas with a diluent gas to provide a known concentration of lesser value than the original. By measuring the volumetric flow rates of each gas stream and knowing the concentration of the original gas to be diluted, one can calculate the final concentration produced by the following equation:

$$C_u Q_u = C_d (Q_u + Q_d)$$

where:

C_u = concentration of undiluted pollutant gas (ppm);
Q_u = volumetric flow rate of undiluted pollutant gas (ml/min);
C_d = final concentration of diluted gas (ppm); and
Q_d = volumetric flow rate of dilution gas (ml/min).

From the above equation, it is important to know or measure the following variables accurately in order to determine the final concentration: C_u, Q_u and Q_d. Knowing these three values and rearranging the above equation, one can calculate the final concentration of the diluted pollutant gas by:

$$C_d = \frac{C_u Q_u}{Q_u + Q_d}$$

C_u is normally provided by the gas manufacturer or through verification by analysis utilizing Federal Reference Methods.

One of the simplest means of measuring volumetric flows is through the utilization of rotameters. If calibrated, rotameters provide a direct correlation of volumetric flow notation. Figure 6.7 displays a typical single dilution system employing rotameters.

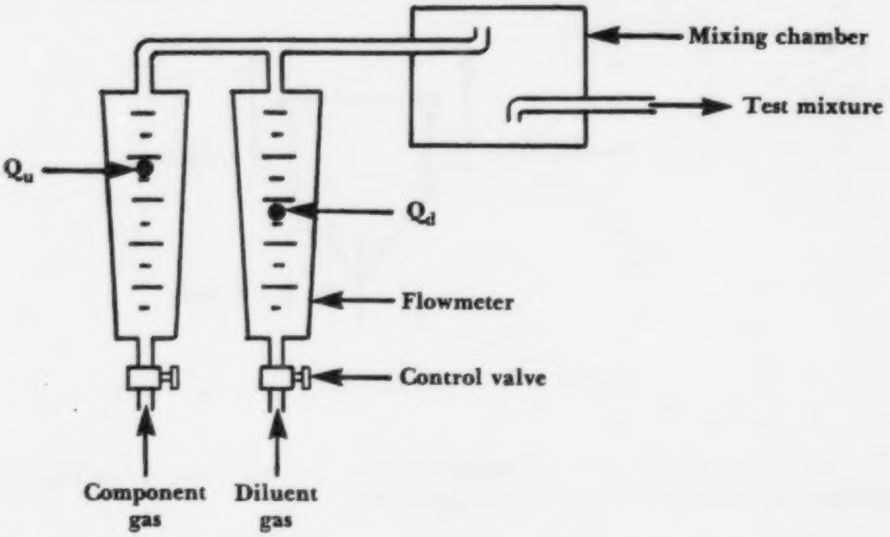

Mixing chamber
Test mixture
Q_u
Q_d
Flowmeter
Control valve
Component gas
Diluent gas

Figure 6.7. Single Dilution System

The rotameter consists of a vertically graduated glass tube and a float located in the tapered vertical tube, as shown in Figure 6.8.

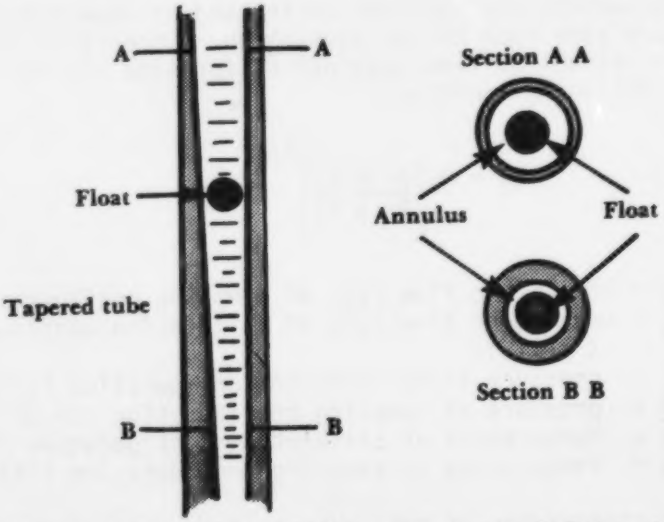

A
A
Section A A
Float
Annulus
Float
Tapered tube
Section B B
B
B

Figure 6.8. Construction of a Typical Rotameter

In operation, the fluid to be measured passes upward through the tapered tube, carrying the float to a position in the tube where its weight is balanced by the upward forces of the fluid flowing past it. At this point, a constant pressure differential across the float is reached and is unique for each rotameter. The forces acting in the upward direction (buoyant and drag forces) exactly equal the force acting in the downward direction (gravity), as displayed in Figure 6.9.

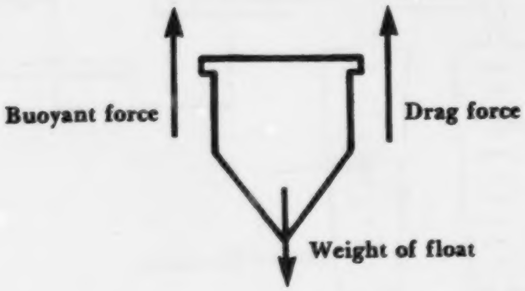


Figure 6.9. Forces Acting on a Float

At this point, the volumetric rate can be read from the graduations etched on the side of the tube.

The rotameter is a secondary standard and must be calibrated before use. When purchased from a manufacturer, a calibration curve is usually provided. They have either calibrated the rotameter against a primary standard, such as a soap-bubble meter, or through knowing construction characteristics of the meter such as tube diameter, float dimensions, float composition and gas characteristics.

Most rotameters are used and calibrated at room temperature with the downstream side open to the atmosphere. Correction for temperature and pressure variations from original calibration configuration are made by the following equation:

$$Q_2 = Q_1\left[\frac{P_1 \times T_2}{P_2 \times T_1}\right]^{1/2}$$

Where: Q_2 = volumetric flow rate of sampling configuration (1/min);
Q_1 = volumetric flow rate of calibration configuration (1/min);
P_1 = pressure at calibration configuration (in Hg);
P_2 = pressure at sampling configuration (in of Hg);
T_1 = temperature at calibration configuration (°F); and
T_2 = temperature at sampling configuration (°F).

Because corrections of this nature are usually cumbersome and inaccurate, rotameters are usually calibrated under sampling conditions.

In recent years, critical orifices have replaced rotameters in monitoring volumetric flow. If operated properly, the critical orifice ensures exact delivery of a gas stream within ± 2%.

The orifice meter consists of some form of restriction located in a tube constructed of glass, metal or other materials. Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop. As a fluid traverses the orifice, a pressure drop develops which can be correlated to flow rate. Figure 6.10 illustrates a simple orifice meter, while Figure 6.11 illustrates a typical orifice meter calibration curve.

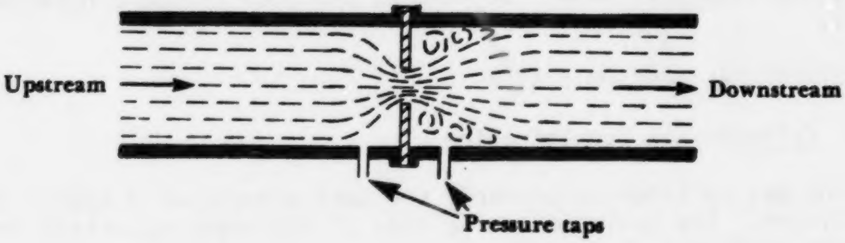


Figure 6.10. Orifice Meter

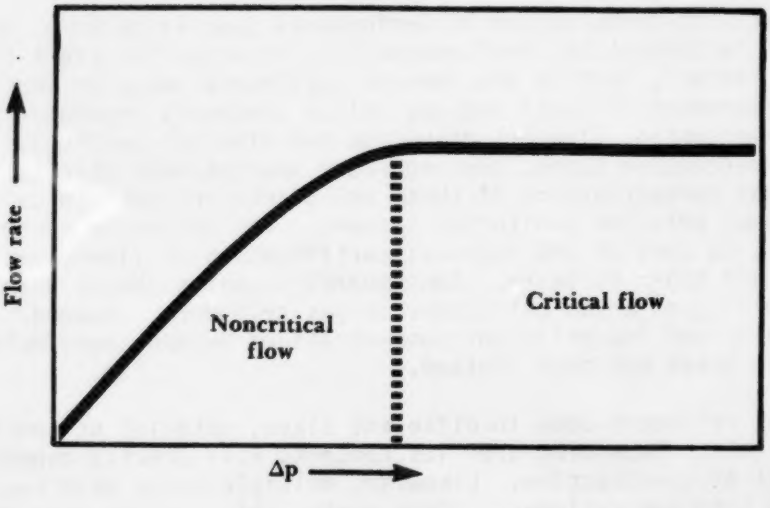


Figure 6.11. Typical Orifice Meter Calibration Curve

As the pressure drop across the orifice increases, flow rates increase, as depicted in Figure 6.11. The region of the calibration curve whose flow rate changes with pressure drop is termed noncritical flow and is associated with a variable orifice meter. Within this region of the calibration curve, one would merely set the pressure drop across the orifice to a desired number to generate a known flow.

If the pressure drop across the orifice is increased until the downstream pressure is equal to approximately 0.53 times the upstream pressure, the velocity of the gas stream becomes sonic. Even if the pressure is increased, no increase in flow will occur. The orifice meter has therefore become "critical." Under these conditions, a constant flow will occur, as long as the 0.53 pressure relationship exists.

6.3 STATIC CALIBRATION SYSTEMS

6.3.1 Cylinder Gas Concentration

The gas cylinder is probably the best example of a static calibration system. The cylinder can be made of different materials and produced in different sizes. The experience of utilizing gas cylinders as an auditing technique has been well established in ambient air monitoring. Highly accurate gas standards for such pollutant as SO_2, NO_x, CO_2, and CO have been used routinely for calibration when auditing ambient air quality monitors. Manufacturers supply gas mixtures which are routinely accompanied with a certificate of analysis and a statement of accuracy. Accuracy levels are generally quoted between 2-5% of the component values.

With the promulgation of Performance Specification 5, sources subject to Subpart BB, Performance Specification for Kraft Pulp Mills, had to install, certify and operate continuous emission monitors for the measurement of total reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl disulfide and dimethyl sulfide). Through the use of permeation tubes, the regulated sources were able to generate different concentrations of these pollutants in order to calibrate their continuous emission monitoring systems. The permeation tube system, however, is complex and requires certification of flowmeters, temperature gauges and other hardware. Consequently, sources began examining the availability of these pollutants in gas cylinders. However, due to the reactivity and low pollutant concentrations needed, manufacture of these cylinder gases has been limited.

Gas cylinders come in different sizes, material of construct and weights. Depending upon its contents will greatly depend upon material of construction. Likewise, multiple gases have been incorporated into one cylinder. Once again, this depends upon reactivity, compressability and stability of the gases.

Cylinders containing a pollutant gas are manufactured by adding a known volume of gas to the cylinder, then pressurizing the cylinder with a diluent gas to a total gas cylinder pressure. The concentration of the gas mixture formed can be calculated by the following equation:

$$c_{ppm} = \frac{10^6 \times V_c}{V_d + V_c} = \frac{10^6 p_c}{p_t}$$

$$c_{\%} = \frac{10^2 \times V_c}{V_d + V_c} = \frac{10^2 p_c}{p_t}$$

c_{ppm} = *concentration of gas mixture, ppm by volume*
$c_{\%}$ = *concentration of gas mixture, percent*
V_c = *volume of contaminant gas*
V_d = *volume of diluent gases*
p_c = *partial pressure of contaminant gas*
p_t = *total pressure of the gas mixture*

This technique of producing gas concentration is fairly accurate to gas concentrations from 50 ppm to more than 6000 ppm, depending on the stability of the gas mixtures.

Another technique of preparing gas cylinder standards is "by-weight". Utilizing this technique the cylinders are evacuated, then filled to a weight and allowed to reach equilibrium with the pollutant. The cylinder is then filled to a final weight with diluent gas. All weighing is performed on a high precision balance. The final concentration is determined by the weight percent of pollutant gas in the gas mixture.

6.3.2 Cylinder Gas Problems

In recent years, gas manufacturers have documented problems associated with maintaining accuracy of prepared certified gas standards. Problems which have been investigated and documented are:

- cylinder material; and
- gas stability.

6.3.2.1 Cylinder Material -

The material of construction of the gas cylinders play an important part in the long term stability of the gas concentration. When reactive gases such as oxides of nitrogen, carbon monoxide or sulfur dioxide are blended in a steel cylinder with an inert balance gas, the concentration can vary with time, temperature and pressure. The mixture's instability is random and is dependent on the condition of the individual cylinders. It has been documented that the instability is a function of gas absorption or reaction with the cylinder walls. Early gas cylinders were constructed of mild steel and consequently laked long term stability. To alleviate this problem, many manufacturers have provided gases in materials of construction other than mild steel. They are:

o Waxed Lined o Steel (Cr-Mo) o Treated Aluminum

Table 6.7 illustrates the long term stability of sulfur dioxide in different cylinder materials of construction.

TABLE 6.7
STABILITY OF SULFUR DIOXIDE (SO_2) IN
SELECTIVE GAS CYLINDERS

Cylinder Type	Original Concentration (ppm)	Analyzed After Two Months (ppm)	Analyzed After Two Years (ppm)
Wax lined	160	140	120
Steel (Cr-Mo)	160	148	132
Treated Aluminum	160	159	157

Another method of decreasing the reactivity between the pollutant gas and cylinder material is to "soak" the cylinder with a high concentration of the reactive gas of interest.

The theory behind this "soaking process" is that with time all of the gas that is going to react with or be absorbed into the cylinder walls will do so during the conditioning period. When the cylinder is put into its final mixing stage any further reaction or absorption will suppossedly be precluded.

This method of preconditioning has met with only limited success. The problem arises when one realizes that what has been absorbed can also be desorbed. When the pressure or temperature of the cylinder changes, the gas that was absorbed during the soaking process can desorb so that the concentration that the cylinder delivers can actually increase. Figure 6.12 represents analysis results on preconditioned cylinders containing 5 ppm nitric oxide in nitrogen as the temperature and pressure of the cylinder was varied. As can be seen from Figure 6.12, the cylinder concentrations tend to increase as desorption takes place.

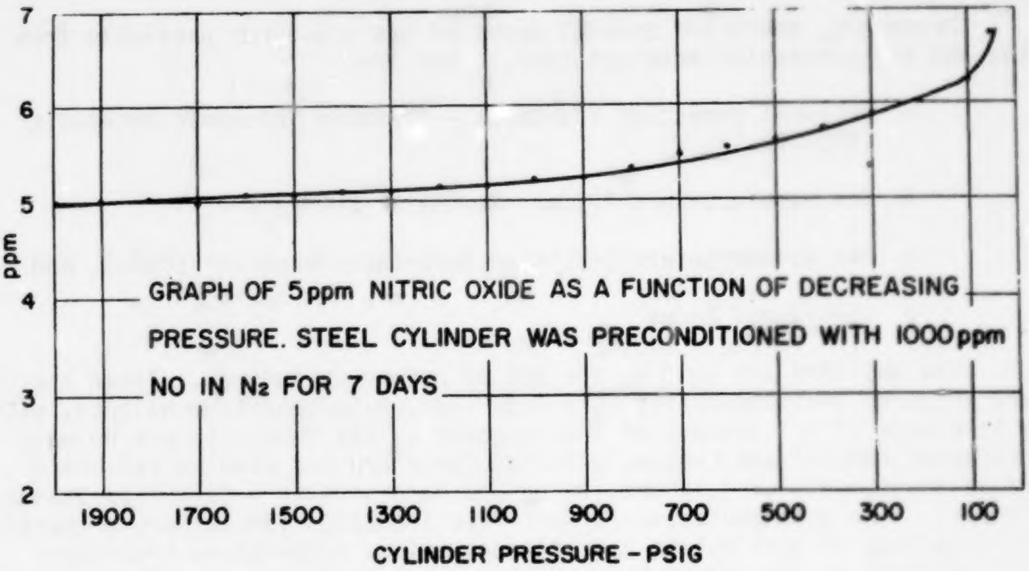


Figure 6.12. Stability of Nitric Oxide in a Pre-Treated Gas Cylinder with Decreasing Pressure

Other techniques such as treating the cylinder surface with a very active gas such as Silane or metal coating of the cylinder walls were equally inefficient. Consequently, the most promising cylinder material appears to be treated aluminum. Treated aluminum cylinder provides a highly inert sealed surface which makes it non-reactive to pollutant gases.

6.3.2.2 Cylinder Gas Stability -

Gas stability is one of the most serious problems associated with certified standards. Gas stability is defined as the ability of a gas mixture to maintain its original concentration with time, temperature or cylinder pressure. Sulfur dioxide is a highly reactive gas which has been found to be unstable at very low concentrations. The instability is due to:

- reaction with moisture;
- reaction with other trace gas impurities; and
- reactions with cylinder walls.

Once again, the use of treated aluminum gas cylinders has enabled manufacturers to provide certified gas mixtures of SO_2 in the 0.1 - 20.0 ppm range.

6.3.3 Cylinder Gas Certification Techniques

Presently, there are several types of gas standards available from the NBS and commercial manufacturers. They are:

- National Bureau of Standards - Standard Reference Materials (NBS-SRMs);
- Gas Manufacturers Primary Standard (GMPS);
- Gas Manufacturers Certified Reference Materials (CRMs); and
- Unanalyzed Gases

The NBS-SRMs are sold by the NBS as primary standards. These standards are prepared environmentally on a high load, high sensitive balance, with a tolerance of ± 1 percent of the component. Gas Manufacturers Primary Standards (GMPSs) are traceable to NBS-SRM's and are used to calibrate those instruments used in certifying Gas Manufacturer's Certified Standards (GMCSs). The Gas Manufacturers Certified Standards (GMCSs) are prepared by a variety of gravimetric and pressure-volume temperature techniques and analyzed by instrumentation which has been calibrated by NBS-SRM's or GMPS's. These standards normally have a certification tolerance of ± 3 percent. The unanalyzed standards are normally prepared in the same manner as the GMCS's, but are not analyzed. Their certification tolerance are normally ± 15 percent.

Table 6.8 summarizes the gas standards available and their associated tolerances.

TABLE 6.8
GAS STANDARDS TOLERANCES

Gas Standard	Tolerance percent of the component
NBS - SRMs	± 1 %
GMPS	± 1 %
GMCS	± 3 %
Unanalyzed	± 15 %
CRM	± 1 % of SRM

6.3.3.1 National Bureau of Standards (NBS) Standard Reference Materials (SRMs)

Standard Reference Materials (SRMs) have been characterized by the National Bureau of Standards for some chemical or physical property and are issued with a Certificate that gives the results of the characteriation. These results are obtained by one of the three methods of certification, i. e. measurement of the property using: (1) a previously validated reference method; (2) two or more independent, reliable measurement methods, or (3) a network of cooperating laboratories, technically competent and thoroughly knowledgeable with the material being tested.

SRM's are defined as being well-characterized and certified materials. They are prepared and used for three main purposes: (1) to help develop accurate methods of analysis (reference methods); (2) to calibrate measurement systems used to: (a) facilitate the exchange of goods, (b) institute quality control, (c) determine performance characteristics or (d) measure some property at the limit of the state-of-the art, and (3) to assure the long-term adequacy and integrity of quality control processes. In these ways, SRM's help ensure the compatibility and accuracy of environmental measurements.

Presently, NBS-SRMs needed in the pulp and paper industry are available for oxygen (O_2) and sulfur dioxide (SO_2). Table 6.9 lists those NBS-SRMs available.

TABLE 6.9

AVAILABLE NBS-SRM PERTINENT TO THE KRAFT PULP MILLS REGULATIONS

SRM	Type	Certified Component	Nominal Concentration
2657	Oxygen in Nitrogen	O_2	2.0 mole percent
2658	Oxygen in Nitrogen	O_2	10.0 mole percent
2659	Oxygen in Nitrogen	O_2	21.0 mole percent
1661a	Sulfur Dioxide in Nitrogen	SO_2	500 ppm
1662a	Sulfur Dioxide in Nitrogen	SO_2	1000 ppm
1663a	Sulfur Dioxide in Nitrogen	SO_2	1500 ppm
1664a	Sulfur Dioxide in Nitrogen	SO_2	2500 ppm
1693	Sulfur Dioxide in Nitrogen	SO_2	50 ppm
1694	Sulfur Dioxide in Nitrogen	SO_2	100 ppm
1696	Sulfur Dioxide in Nitrogen	SO_2	3500 ppm

6.3.3.2 Certified Reference Materials (CRMs) -

Standard Reference Materials (SRMs) and Certified Reference Materials (CRMs) are gaseous standards developed by the National Bureau of Standards (NBS) in cooperation with the Environmental Protection Agency (EPA). The main objective of this program was to help supply gaseous standards to industry without depleting the SRM stock. NBS could neither increase production nor allow "out-of-stock" situations to develop with their SRM inventory. Consequently, a method was developed which enabled the specialty gas industry to produce accurate gas standards while maintaining traceability to NBS-SRM's. The new CRM's would duplicate SRMs in stock in regard to stability, homogeneity and concentration.

In brief, CRM's are certified by the manufacturer by analyzing their concentration by an analyzer that has been calibrated with SRM's. The idea is to calibrate the analyzer with two or three SRM's, then analyze a "batch" of CRMs with the calibrated analyzer. This provides traceability to NBS-SRM's and increases the number of reference gases available for commercial usage.

The process by which CRM's are prepared and certified involve:

- preparation of the "batch" CRMs;
- demonstration of homogeneity and stability of the batch;
- batch analysis;
- audit by an independent lab; and
- review of procedures and analytical data by NBS.

If the CRMs meet all the requirements, then the CRMs are certified reference gases to NBS-SRMs.

6.3.3.2.1 Preparation of CRMs -

CRM's must be prepared in gas cylinders of 10 or more at one time by a continuous gas generating system followed by a simultaneous compression system. The concentration of the gases in the cylinder must be identical and must lie within ± 1% of the concentration of the existing SRM which the gas manufacturer must physically possess. This stipulation is required because the CRM program was developed to extend the supply of available SRMs and to minimize systematic and random errors during analysis if the CRM is close in concentration to the SRM. (The SRM will be used as one of the standards in developing the calibration curve for the analyzer upon which the CRM concentration will be determined).

6.3.3.2.2 Demonstration of Homogeneity and Stability -

Homogeneity and stability of the batch of 10 gas cylinders or more are determined by analyzing the batch soon after preparation. The batch is then "incubated" for a period of 30 days. The batch is then reanalyzed and the results from the first batch are compared to the results of the second batch to determine their stability. The difference should be random and the algebraic sum of the difference should be small. The homogeneity of the batch is determined by examining the differences between the concentration of the sample gases and comparing them to the expected differences based on the precision of the method.

6.3.3.2.3 Batch Analysis -

The concentration of each CRM (gas cylinder) in the batch is determined with an analyzer that has been calibrated utilizing the existing SRM as one of the calibration points. The response of the analyzer to the SRM calibration points is observed and a calibration curve is constructed. The CRM's concentrations are then determined by the analyzer utilizing the calibration curve generated from the SRMs. The analysis must confirm that the concentration of each of the CRMs lies within ± 1% of the concentration of the SRM that is being duplicated.

6.3.3.2.4 Audit By An Independent Lab -

Two of the CRMs produced by the manufacturer must be analyzed by an independent lab by an analyzer that has been calibrated by SRMs. The results of this effort are sent to NBS for evaluation.

6.3.3.2.5 Review of Procedures and Analytical Data by NBS -

The results of the manufacturers analysis of stability and homogeneity along with individual gas cylinder analysis are sent to NBS for review. Concurrent with this, the independent lab sends its results to NBS. From this information, NBS determines whether the "batch" are certified CRMs.

6.3.3.2.6 Availability of CRMs -

Presently, thirty (30) batches of CRMs have been approved by NBS for sale. These batches contain carbon monoxide in nitrogen or air and nitric oxide in nitrogen. The addition of SO_2 in nitrogen to the available CRM list will occur late 1985. Table 6.10 lists those CRMs which are available along with their manufacturer.

TABLE 6.10
AVAILABLE CRMs AND THEIR MANUFACTURER

CRM Gas Type and Concentration	Gas Manufacturer
1. Carbon Monoxide in N_2 10 ppm 25 ppm 50 ppm 250 ppm 1000 ppm 2500 ppm 5000 ppm	Scott Specialty Gases Scott Environmental Technology, Inc. U. S. Route 611 Plumsteadville, Pa. 18949 Telephone: (215) 766-8861
25 ppm 50 ppm 100 ppm 250 ppm 500 ppm 1000 ppm 2500 ppm 5000 ppm 4 percent 8 percent	AIRCO Industrial Gases River and Union Landing Roads Riverton, N. J. 08077 Telephone: (609) 829-7878
10 ppm 50 ppm	Matheson 30 Seaview Drive Secaucus, N. J. 07094 Telephone: (201) 867-4100
50 ppm 500 ppm 5000 ppm 1 percent 2 percent 8 percent	Air Products & Chemicals, Inc. P. O. Box 351 Tamaqua, PA 18252 Telephone: (717) 467-2981
2. Carbon Monoxide in Air 48 ppm	AIRCO Industrial Gases (See above for address and telephone)
48 ppm	Scott Specialty Gases (See above for address and telephone)
3. Nitric Oxide in Nitrogen 100 ppm 250 ppm 500 ppm	AIRCO Industrial Gases (See above for address and telephone)
250 ppm	Scott Specialty Gases (See above for address and telephone)

6.3.3.3 Environmental Protection Agency (EPA) Protocol No. 1 Gases -

EPA Protocol No. 1, Traceability Protocol for Establishing True Concentrations of Gases Used For Calibration and Audits of Continuous Source Emission Monitors, provides for a direct comparison between the calibration and audit gas standards and an NBS-SRM or gas manufacturer's primary standard (GMPS) which is referenced to NBS-SRM. The traceability procedure is intended to minimize errors in determining the true concentration of a cylinder gas. Protocol No. 1 is very similar to the CRM procedures except:

- Protocol No. 1 allows use of GMPS whereas CRM procedures do not;
- Protocol No. 1 allows the user to certify his own cylinders if he follows the protocol; and
- The gas cylinder does not have to be within ± 1% of the SRM (or GMPS).

6.3.3.3.1 Concentration Determination -

The procedure of determining the "true" concentration of the gas cylinder involves the following steps:

- development of a calibration curve utilizing two NBS-SRMs;
- daily span check utilizing NBS-SRMs or GMPs;
- cylinder analysis; and
- cylinder gas stability

Calibration Curve Development

A multipoint calibration curve is prepared monthly using two SRM cylinder gases and a zero gas. (The zero gas must not contain more than 1.2% of the full scale concentration of the component being analyzed). The multipoint calibration is accomplished by diluting the highest SRM with zero gas using a calibration flow system. The instrument response for 6 points representing 0, 10, 30, 50, 75 and of the instrument full scale is obtained. The data is plotted and calibration curve is developed. The instrument response for the other lower SRM, without dilution, is obtained. The apparent concentrations from the calibration curve to the true concentration of the lower SRM is compared. If the difference between the apparent concentration and the true concentration of the lower SRM exceeds 3% of the true concentration, then the multipoint calibration procedure must be repeated.

Daily Span Check

On the day the gas cylinder is to be analyzed, the instrument response is compared to the two SRMs (or GMPS) in the range of the calibration gas to be analyzed and a zero gas. First, the zero gas is injected into the analyzer and the zero adjusted to the appropriate concentration. Then the highest SRM or GMPS is injected into the analyzer and the span valve adjusted to the valve obtained in the most recent multipoint calibration. Finally, the lower SRM (or GMPS) is injected into the analyzer. If the response to the lower SRM (or GMPS) varies by greater than 3% from the response obtained in the most recent multipoint calibration, a full multipoint calibration must be performed. If the response to the lower SRM (or GMPS) is within 3%, then the instrument is ready to analyze the gas cylinder.

Cylinder Analysis

The analysis involves the direct comparison between the gas cylinder and the SRM (or GMPS). This allows for compensation for variation in instrument response between the time of daily span check and the time of analysis.

The analysis is performed by alternatively injecting the calibration gas cylinder, then the SRM (or GMPS) until three pairs of analyses have been completed. For this, the true concentration of the cylinder gas is determined by the following equation:

$$\begin{array}{c}\text{True Concentration}\\ \text{of}\\ \text{Gas Cylinder}\end{array} = \left[\begin{array}{c}\text{Apparent Conc.}\\ \text{of}\\ \text{Gas Cylinder}\end{array}\right] \times \left[\frac{\text{True Conc. of SRM (or GMPS)}}{\text{Appar. Conc. of SRM (or GMPS)}}\right]$$

The mean of the three values determines the true concentration of the gas cylinder. No one valve can differ from the mean by greater than 1.5%.

6.4 VERIFICATION OF CYLINDER GAS CONCENTRATION

Concurrent with Federal Regulation, Appendix B and F of Part 60, Standards of Performance for New Stationary Sources, the source owner must verify gas cylinder concentration used in the CEM program by either purchasing cylinder gases which conform to EPA's traceability protocol or analyze the cylinder gases by Federal Reference Methods. The traceability procedure for gases used in calibrating and auditing continuous emission monitors is intended to minimize systematic and random errors during the analysis of these gases and to establish the true concentration by means of National Bureau of Standards, Standard Reference Materials (NBS, SRM). As previously discussed, the procedure provides for a direct comparison between the calibration and audit gas standards and an NBS, SRM or a gas manufacturers primary standard (GMPS) which is referenced to NBS, SRM.

The regulations allow for the source owner to verify his gas cylinder concentration by utilizing the Federal Reference Methods. For SO_2 gas cylinders, this would involve sampling and analysis using Federal Reference Method 6, Determination of Sulfur Dioxide Emissions From Stationary Sources. For H_2S, Federal Reference Method 11, Determination of Hydrogen Sulfide Content Of Fuel Gas Streams in Petroleum Refineries, is utilized.

In recent years, U. S. EPA has examined procedures for analyzing gas cylinders utilizing Federal Reference Methods. Studies have indicated an average error of ± 5% for three consecutive measurements employing the Reference Methods. Three gas cylinder sample collection procedures were evaluated: They were:

(1) direct pressure;
(2) vented bubbler; and
(3) evacuated flask.

Of the three procedures, the direct pressure technique appears to be most applicable to gas cylinder concentration determination for SO_2 and H_2S utilizing the Reference Methods.

6.4.1 Certification of Sulfur Dioxide (SO_2) Cylinder Gas -

The direct pressure technique utilizes Federal Reference Method 6 sampling equipment and analysis. The only difference is the pump is bypassed in the meter box because the gas cylinder will provide the pressure needed. Figure 6.13 illustrates the components of the train assembly as used in certification of sulfur dioxide cylinder gases.

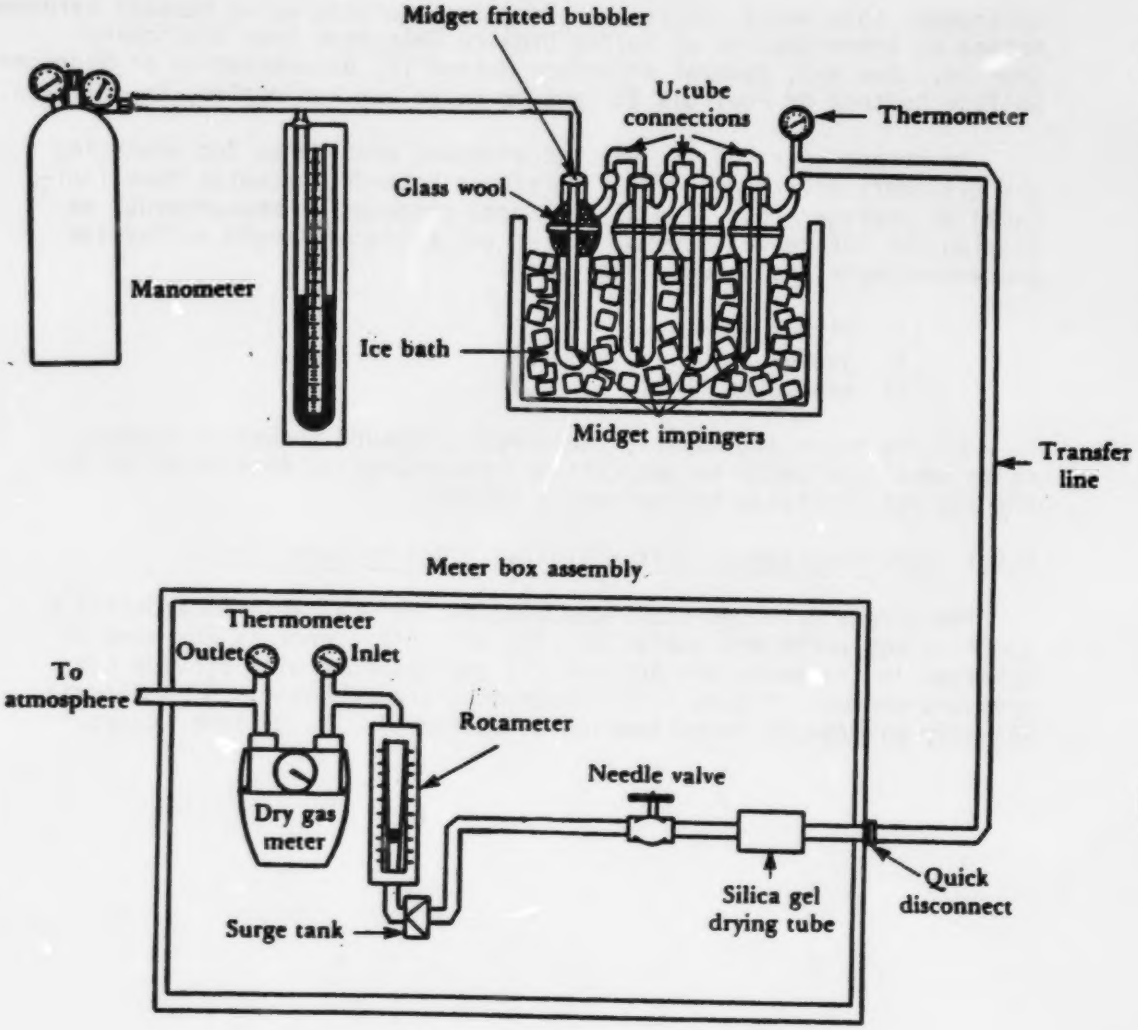

Midget fritted bubbler
U-tube connections
Thermometer
Glass wool
Manometer
Ice bath
Midget impingers
Transfer line
Meter box assembly
Thermometer
Outlet
Inlet
To atmosphere
Rotameter
Needle valve
Dry gas meter
Silica gel drying tube
Quick disconnect
Surge tank

Figure 6.13. SO_2 Cylinder Gas Certification Set-up

The sampling train consists of a U-tube manometer, an impinger train and a meter box assembly. The U-tube manometer is used to monitor system pressure at the inlet of the first impinger.

The bubbler and impingers consist of one midget bubbler with the top packed with glass wool connected in series with three midget impingers. The bubbler and impingers must be connected in series with leak free glass connections.

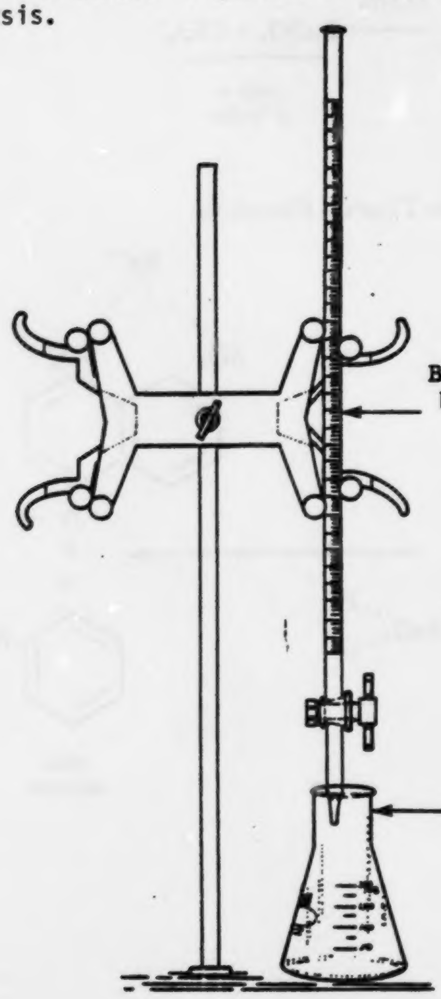
The metering system should consist of a vacuum gage; thermometers capable of measuring temperature in the dry gas meter; and a dry gas meter with 2% accuracy at the required sampling rate.

In essence, a gas cylinder is certified by measuring the absorbed SO_2 in the hydrogen peroxide impingers after a stated sampling period.

Chemically, during sampling, the SO_2 in the gas stream is oxidized by the hydrogen peroxide impingers by the following reaction:

$$\underset{\text{Sulfur Dioxide}}{SO_2} + \underset{\text{Hydrogen Peroxide}}{H_2O_2} \longrightarrow \underset{\text{Sulfuric Acid}}{H_2SO_4}$$

The sample train impingers are recovered, diluted to a known volume and titrated with standardized barium perchlorate reagent using thorin as the indicator. The indicator changes from yellow to pink when the endpoint is reached. Figure 6.14 displays the titration set-up for the analysis.



Burette standardized barium-containing perchlorate [$Ba(ClO_4)_2$]

Flask:
- **80 mL of 100% IPA**
- **20-mL of sample**
- **2-4 drops thorin indicato**

Figure 6.14. SO_2 Analysis Set-up

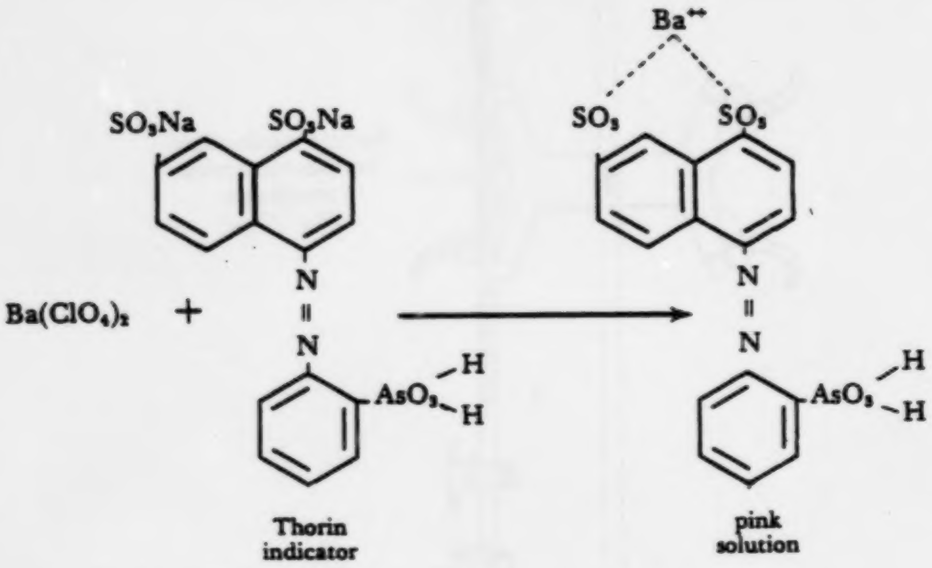
The titration involves reacting the standardized barium perchlorate with the formed sulfuric acid to precipitate barium sulfate. At this point, the indicator is still yellow. When all of the available sulfate (SO_4) has precipitated as $BaSO_4$, the barium attacks the thorin indicator, changing the color from yellow to pink.

Chemically, this can be expressed as:

Sulfate Reaction

$$Ba(ClO_4) + H_2SO_4 \xrightarrow{\text{Thorin}} \underbrace{BaSO_4 + ClO_4^-}_{\text{yellow solution}}$$

Barium-Thorin Reaction


Ba⁺⁺
SO₃Na
SO₃Na
SO₃
SO₃
N
N
N
N
Ba(ClO₄)₂
+
AsO₃
H
H
AsO₃
H
H
Thorin indicator
pink solution

This reaction of the standardized barium with the sulfate ion provides a direct correlation between the formed sulfate in the impinger and the SO_2 in the gas cylinder.

The concentration of the SO_2 in the gas cylinder can then be calculated from the titration by the following equation:

$$c_{SO_2} = K_2 \frac{N(V_t - V_{tb}) \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Where: c_{SO_2} = emission rate of sulfur dioxide (lb/scf)
V_t = volume of titrant required for sample (mL), $Ba(ClO_4)_2$
V_{tb} = volume of titrant required for blank (mL), $Ba(ClO_4)_2$
N = normality of $Ba(ClO_4)_2$ (meq/mL)
V_{soln} = total volume of sample (mL)
$V_{m(std)}$ = volume of sample corrected to standard conditions (dscf)
V_a = volume of aliquot titrated (mL)
$K_2 = 7.061 \times 10^{-5}$ lb/meq

$$c_{SO_2} = (7.061 \times 10^{-5}) \left[\frac{(\underline{\qquad})(\underline{\quad} - \underline{\quad})\left(\frac{\underline{\qquad}}{\underline{\qquad}}\right)}{(\underline{\qquad})} \right]$$

$$= \underline{\qquad\qquad} \text{ lb/scf}$$

The concentration of SO_2, in ppm, can then be calculated from the following equation:

$$SO_2(\text{ppm}) = 6.01 \times 10^6 (c_{SO_2})$$

Where: c_{SO_2} = SO_2 concentration in lb/scf
6.01×10^6 = conversion factor (lb/dscf to μL/L)

$$c_{SO_2} = (6.01 \times 10^6)(\underline{\qquad})$$

$$= \underline{\qquad\quad} \text{ ppm}$$

The analysis is performed in triplicate along with an EPA certified vial. The average is used to determine concentration of the gas cylinder.

6.4.2 Certification of Hydrogen Sulfide (H_2S) Cylinder Gas

Similar to SO_2 procedures, H_2S is determined utilizing Federal Reference Method 11 sampling equipment and analysis. Figure 6.15 illustrates the components of the certification train assembly.

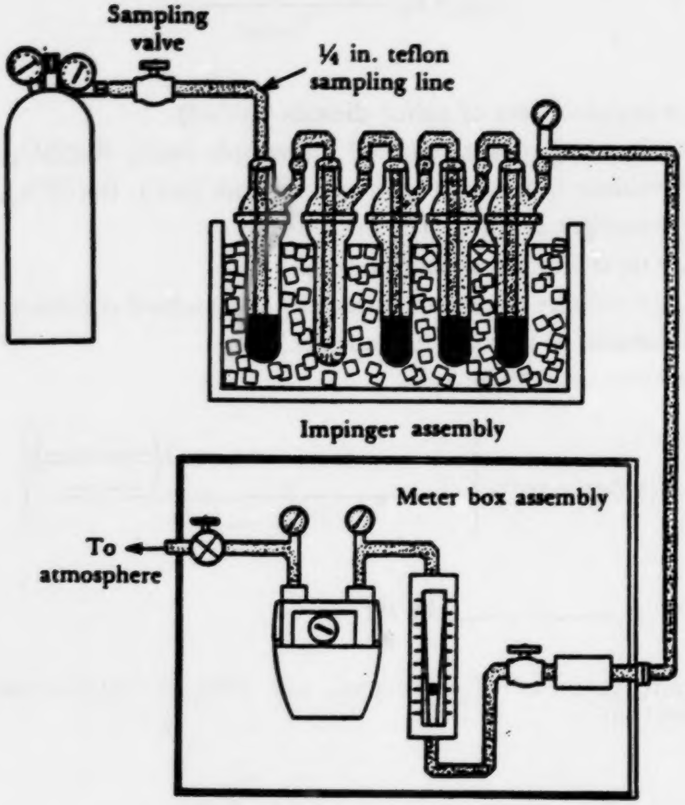

Sampling valve
¼ in. teflon sampling line
Impinger assembly
Meter box assembly
To atmosphere

Figure 6.15. H_2S Cylinder Gas Certification Set-up

The sampling train consists of 5 midget impingers connected in series, each with 30 mL capacity. The metering system should consist of a vacuum gage, a rate meter, and a dry gas meter with 2% accuracy at the required sampling rate. A U-tube water manometer is also used to perform a leak rate determination.

The five TRS detectors under evaluation were:

- Detector 1: Gas Chromatography with Flame Photometry;
- Detector 2: ITT Barton Coulometric Titrator;
- Detector 3: Thermal Oxidation with ITT Barton Coulometric Titrator;
- Detector 4: Photoionization; and
- Detector 5: Flame Photometry Total Sulfur Analyzer.

The gas chromatography technique (Detector 1) with flame photometric analysis involved analytical separation of all reduced sulfur compounds by chromatographic columns with subsequent analysis. Detector 2 (coulometric titration) involved analysis of all reduced sulfur compounds with no pretreatment. Detector 3 configuration involved pretreatment of the gas sample by thermal oxidation of all reduced sulfur compounds to SO_2, then analysis by the coulometric titration technique. Detector 4 (photoionization technique) and Detector 5 (flame photometric technique) required no sample pretreatment. However, due to component failure, the photoionization technique provided little information during the test series.

Before the accuracy of the individual detector systems could be examined, NCASI evaluated the conditioning system to pass reduced sulfur compounds and the response time of the total TRS CEM system.

7.2.2 Conditioning System Evaluation to Pass Reduced Sulfur Compounds

To determine the efficiency of the conditioning system to pass reduced sulfur compounds, known concentrations of H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$ were injected at the probe inlet and allowed to pass through the conditioning system to the detectors. Fifteen (15) tests were performed at total reduced sulfur concentrations ranging from 2.6 ppm to 5.8 ppm. The results of this portion of the field study indicated that a properly maintained conditioning system can pass greater than 90% of reduced sulfur compounds at an average inlet concentration of 4.8 ppm. These results, however, are applicable only to Kraft recovery furnaces as reported by NCASI. Greater sample losses were experienced at lime kilns (~75% reduced sulfur compounds pass at a ~10 ppm inlet concentration).

7.2.3 Sampling System Response Time

Sampling system response time was measured with the ITT Barton coulometric titrator. The upscale and downscale values were determined according to Performance Specification Test 2 and 3. These tests indicate an average monitor response time of 7.2 minutes, well within the 15 minutes allowed by the Performance Specification Test.

7.2.4 Detector Accuracy and Zero/Calibration Drift

7.2.4.1 Accuracy Determination -

The accuracy of each system was compared to that of the others (in some cases) and routinely compared to the gas chromatograph with flame photometric detection as the reference method. To determine accuracy, the detectors were turned on each day, zeroed with zero air and calibrated. The accuracy tests were then determined for a test period of 8 to 14 hours. This protocol was established by NCASI due to the calibration drift problems associated with the gas chromatograph.

The results of the accuracy tests are presented in Table 7.1. The results indicated the Barton coulometric titrator, used in its normal mode and in association with the thermal oxidation system, was the only system which operated according to manufacturer specifications and within EPA guidelines.

TABLE 7.1

NCASI DRIFT/ACCURACY EVALUATION
OF TRS DETECTORS - STUDY #1

Detector	Range, ppm	# of Observations	Avg. Diff. between Obs. (ppm)	% Within[2] Range, ppm $-1.5 \le$ Difference ≤ 1.5	Accuracy (%)
Coulometric Titrator	0-5	326	0.04	100.0	5.3
Coulometric Titrator	5-30	126	0.11	68.6	5.8
Thermal Oxidation System	5-30	119	0.05	70.0	6.0
Flame Photometric Total Sulfur Analyzer	5-30	20	- 1.34	Unreported	20.5
Photoionization Detector[3]	-	-	-	-	-

[1] $$\%\ \text{Accuracy} = \frac{[\text{Mean Difference (Absolute)} + 95\%\ \text{C.I.}]}{[\text{Mean Reference Method Value}]} \times 100$$

[2] 24-hour zero/calibration drift limits, as specified in Performance Specification Test 5.

[3] No useful information due to component failure.

During sampling, the hydrogen sulfide gas in the gas cylinder is scrubbed by the cadmium sulfate in the impingers to form a yellow precipitate, CdS. Chemically, this can be expressed by the following equation:

$$\underset{\substack{\text{Hydrogen}\\\text{Sulfide}}}{H_2S} + \underset{\substack{\text{Cadmium}\\\text{Sulfate}}}{CdSO_4} \longrightarrow \underset{\substack{\text{Cadmium}\\\text{Sulfide}}}{CdS} + \underset{\substack{\text{Sulfuric}\\\text{Adic}}}{H_2SO_4}$$

After sampling, the impingers are recovered into a 500-ml iodine numbered volumetric flask containing acidified iodine solution. The acidified iodine solution liberates the captured H_2S which then reacts with the available iodine. Chemically, the following reactions are occurring:

$$\underset{\substack{\text{Cadmium}\\\text{Sulfate}}}{CdS} + \underset{\substack{\text{Hydrogen}\\\text{Chloride}}}{2HCl} \longrightarrow \underset{\substack{\text{Hydrogen}\\\text{Sulfate}}}{H_2S} + \underset{\substack{\text{Cadmium}\\\text{Chloride}}}{CdCl_2}$$

$$\underset{\substack{\text{Hydrogen}\\\text{Sulfide}}}{H_2S} + \underset{\text{Iodine}}{I_2} \longrightarrow \underset{\substack{\text{Hydrogen}\\\text{Iodine}}}{2HI} + \underset{\text{Sulfur}}{S}$$

The remaining iodine in the flask is titrated with standardized sodium thiosulfate using starch as the indicator. The titration is from a dark purple to clear endpoint.

This titration process has completed the following reaction:

$$\overset{\text{Dark Blue}}{\underset{\substack{\text{Standardized}\\\text{Sodium Thiosulfate}}}{2Na_2S_2O_3 + I_2}} \xrightarrow{\text{starch}} \overset{\text{Clear}}{Na_2S_4O_6 + 2NaI}$$

By analyzing a blank solution of acidified iodine and comparing the titrated sample to the blank sample, the concentration of H_2S in the gas cylinder can be determined by the following equation:

$$c_{H_2S} = K \frac{(V_{IT}N_I - V_{TT}N_T)\text{sample} - (V_{IT}N_I - V_{TT}N_T)\text{blank}}{V_{m(std)}}$$

Where: c_{H_2S} = emission rate of H_2S at standard conditions, gr/dscf
K = conversion factor

$$= \frac{(34.07 \text{ g/mole } H_2S)(7000 \text{ gr/lb})}{(2H_2S \text{ eq/mole})(1000 \text{ mL/L})(453.6 \text{ g/lb})} = 0.2629$$

V_{IT} = volume of standard iodine solution = 50 mL
N_I = normality of standard iodine solution, g-eq/L
V_{TT} = volume of standard sodium thiosulfate solution, mL
N_T = normality of standard sodium thiosulfate solution g-eq/L
$V_{m(std)}$ = dry gas volume at standard conditions, dscf

The concentration of H_2S, in ppm, can be calculated from the following equation:

$$H_2S(\text{ppm}) = (K)(c_{H_2S})$$

Where: c_{H_2S} = emission rate of H_2S at standard conditions, gr/dscf
K = conversion factor

$$= (0.0001429 \text{ lb/gr})(453.6 \times 10^6 \mu\text{g/lb})(\mu \text{ mole}/34\mu\text{g})$$

$$(22.4 \ \mu\text{l}/\mu\text{mole})(\text{dscf}/28.317 \text{ L})\left(\frac{293\,°R}{273\,°R}\right)$$

$$= 1.62 \times 10^3$$

$$= (1.62 \times 10^3)(\underline{\qquad\qquad})$$

$$= \underline{\qquad\qquad} \text{ ppm } H_2S$$

Similar to SO_2 determination, three analysis are used to calculate cylinder concentration.

7.0 COMPARATIVE STUDIES OF TRS MONITORS

7.1 INTRODUCTION

Since the early 1960s, the National Council for Air and Stream Improvement (NCASI) has conducted several studies associated with the development and evaluation of measurement techniques for total reduced sulfur from pulp mill processes. Early in the evaluation, the studies centered around manual extractive techniques. However, as continuous emission monitors started playing a predominant role in a source emission monitoring program, the NCASI turned its attention to their performance and evaluation. The objective of this chapter is to examine three major studies involving TRS CEM evaluations performed by the NCASI. The first study was conducted in 1977 and dealt with TRS detector evaluation. The second study, conducted in 1983, evaluated six (6) commercially available TRS monitors. Finally, the third study involved comparison between gas chromatography (Reference Method 16) and wet chemical (Reference Method 16A) techniques.

7.2 NCASI EVALUATION OF TRS DETECTORS - STUDY #1

The first major study by NCASI involved evaluating commercially available TRS CEMs. The objective of this 1977 study was two fold: (1) to observe the field performance of several TRS monitoring detectors in reference to their accuracy, zero and span drift over a period of time; and (2) to evaluate the performance of a properly designed recovery furnace sampling system by determining its response characteristics.

The study was conducted over a period of 3 months in two district phases. During the first phase, the sampling system was installed and the performance of the commercially available TRS monitor detectors was evaluated. Those systems evaluated during this phase involved gas chromatography, coulometric titration and photoionization detection. During the second phase of the study, the source gas was oxidized to SO_2 and measured as SO_2 on a flame photometric total sulfur analyzer. Results of that study were reported in Atmospheric Quality Improvement Technical Bulletin No. 91, published by the NCASI.

7.2.1 Test Configuration

The objective of the study was to examine commercially available TRS detector systems, not their extractive mechanism. As such, a common sample extraction/conditioning system was used. The sample extraction/conditioning system consisted of an external filtered probe, a condenser, a continuous SO_2 liquid scrubber system and a sample manifold, as illustrated in Figure 7.1.

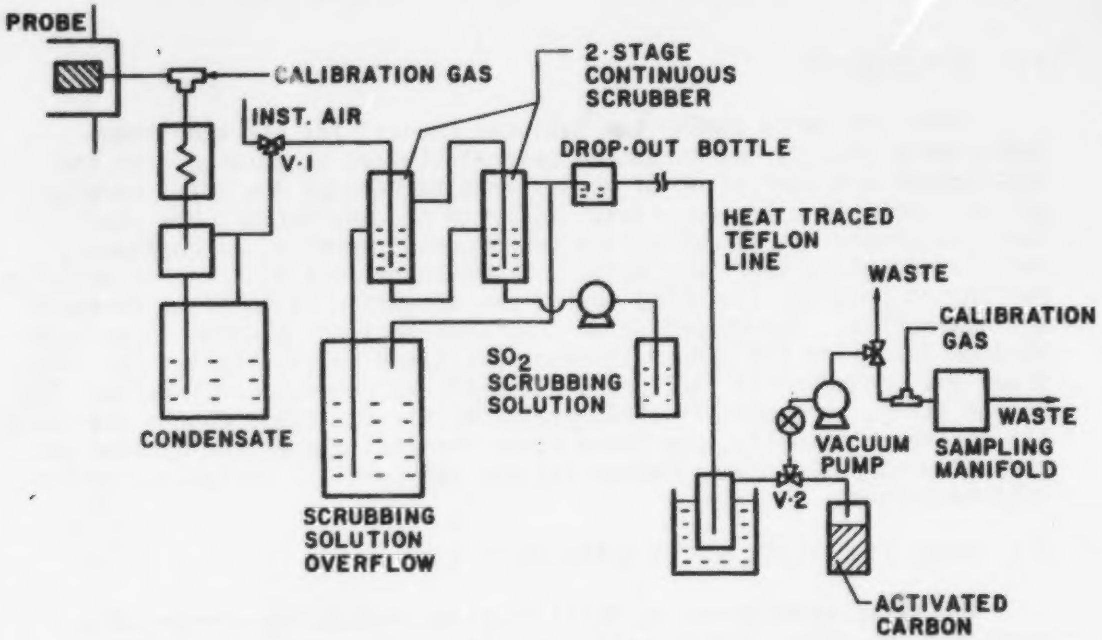

PROBE
CALIBRATION GAS
INST. AIR
V·1
2·STAGE CONTINUOUS SCRUBBER
DROP·OUT BOTTLE
HEAT TRACED TEFLON LINE
WASTE
CALIBRATION GAS
WASTE
SAMPLING MANIFOLD
VACUUM PUMP
V·2
SO_2 SCRUBBING SOLUTION
CONDENSATE
SCRUBBING SOLUTION OVERFLOW
ACTIVATED CARBON

Figure 7.1. Common Extraction System Used in the NCASI TRS Detector Evaluation.

From the manifold, the gas stream was split into five individual streams leading to the five detectors, as illustrated in Figure 7.2

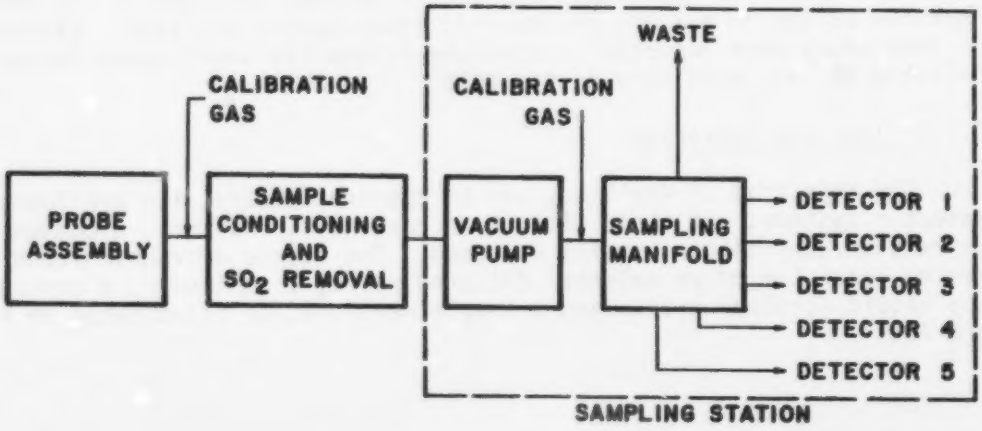

WASTE
CALIBRATION GAS
CALIBRATION GAS
PROBE ASSEMBLY
SAMPLE CONDITIONING AND SO_2 REMOVAL
VACUUM PUMP
SAMPLING MANIFOLD
DETECTOR 1
DETECTOR 2
DETECTOR 3
DETECTOR 4
DETECTOR 5
SAMPLING STATION

Figure 7.2. Sampling Manifold Configuration Leading to Individual Detectors.

7.2.4.2 Zero and Span Drift Determination -

A 24-hour zero/span drift determination was performed, according to Performance Specification Test 2, on the coulometric titrator detection principle. The results of this evaluation indicated 1.27% and 9.78% span drift values for the 24-hour zero/span determination, respectively.

7.2.5 Test Results Summary

Results of the first major study of commercially available TRS detectors indicate that both the Barton coulometric titrator (operated in its normal mode) and a thermal oxidation system used in conjunction with the Barton coulometric titrator operated within EPA's guidelines at Kraft recovery furnaces.

7.3 NCASI EVALUATION OF TRS DETECTORS - STUDY #2

7.3.1 Introduction

Since that evaluation, two important events occurred to cause NCASI to initiate a second study. In 1981, EPA proposed Performance Specification 5 which involved performance specifications associated with calibration drift and relative accuracy of installed TRS monitors. Likewise, since the 1977 study, several new manufacturers were providing TRS monitors on a commercial basis to the Kraft pulp mill industry. With very little information associated with the newer instruments, NCASI, in June 1983, began a six-month test to evaluate available TRS CEMs.

The main objective of this 1983 study was to evaluate commercially available TRS monitors and their detection systems. The objective was not to evaluate the probe or conditioning system associated with each monitoring system. As part of the study, six manufacturers of TRS monitors were evaluated. They were:

- Candel Dynalyzer Series 300 Portable TRS Analyzer:
- ITT-Barton Model 411-S TRS Monitoring System;
- Modified Monitor Labs Model 8850 SO_2 Monitor;
- Sampling Technology Incorporated (STI) Model 100 TRS Monitor;
- Theta Sensors Model 7000 SO_2 Monitor; and
- Tracor Atlas Model 825 R-D Analyzers.

Table 7.2 lists those monitors that were evaluated and their measurement principles.

TABLE 7.2
NCASI EVALUATION OF TRS DETECTORS - STUDY #2

Manufacturer	Detection Principle	TRS Analyzed As	Conditioning System	
			Thermal Oxidation	Reduction Furnace
Candel Dynalyzer Series 300 Portable TRS Analyzer P.O. Box 2580 Sidney, British Columbia	Electrochemical	SO_2	Quartz Tube	N/A
ITT - Barton Model 411 TRS Monitor P.O. Box 1882 City of Industry, CA	Coulometric Titrator	SO_2	Quartz Tube	N/A
Monitor Labs Model 8850 SO_2 Analyzer	Fluorescent	SO_2	Stainless Steel Tube (Stainlesss Steel Chips) 300°C	N/A
STI Model 100 TRS P.O. Box B Waldron, AR	Fluorescent	SO_2	Quartz Tube (1500°F)	N/A
Theta Sensors Portable TRS Monitor 17635A Rowland Street La Puente, CA	Electrochemical	SO_2	Not supplied by Manufacturer	N/A
Tracor Atlas Model 856/825 TRS Monitor	Impregnated Lead Acetate	Total Reduced Sulfur (H_2S)	N/A	Hydrogenator Reduction Furnace (1000°C - 1300°C)

All analyzers were evaluated in five (5) major categories:

- Operating and maintenance experience;
- Thermal oxidation furnace design and performance;
- Tests of interferences from NO and CO_2;
- Calibration drift test; and
- Relative accuracy test.

7.3.2 Test Program

The test program involved both laboratory and field evaluation of the TRS monitors only and not the complete sampling system. The laboratory evaluation occurred at the NCASI Gainesville Regional Office. The field evaluation occurred at a local Combustion Engineering Kraft recovery furnace with a rated capacity of 130,000 lbs/hr of oxidized black liquor at 65% solids. The furnace had a cascade evaporation and two wet bottom precipitators in series. The sulfide level in the oxidized black liquor ranged from 0 to 0.5 gm/l as Na_2S. The particulate concentration in the stack gas was normally 0.02 gr/DSCF.

The TRS CEM evaluation consisted of three major phases;

Phase 1: Survey of TRS CEMs in the industry;

Phase 2: Laboratory/field evaluation of selected monitors; and

Phase 3: Field evaluation of selected probe and gas conditioning system.

The laboratory objectives were to operate the monitors in a controlled environment to gain operating experience. Next, they were challenged with different sulfur compounds to determine furnace ability to oxidize the reduced sulfur compounds to SO_2. The third portion of the laboratory test was to challenge the monitors with NO and CO_2 to determine their interference potential on the monitoring systems.

The field evaluation involved both a calibration drift determination and relative accuracy evaluation. Calibration drift and relative accuracy were determined against Federal Reference Method 16.

7.3.2.1 Laboratory Evaluation -

One of the objectives of the laboratory evaluation was to gain experience in operating the different TRS CEMs in a controlled environment. NCASI reported no major problems associted with operating the instruments on a daily basis. Secondly, the monitors were checked for converter efficiency (TRS ➡ SO_2). As illustrated in Table 7.3, problems were observed with this portion of the evaluation. Where needed, corrective action was taken by NCASI to improve the converter systems. The third objective of the laboratory evaluation was to determine if other gases, i.e. NO and CO_2, interfere with the individual measurement techniques.

The results, summarized in Table 7.3, indicate there was no interference associated with CO_2. However, several monitors showed positive interference from NO gas. Of those monitors evaluated, the electrochemical techniques showed the highest degree of interference. Table 7.3 summarizes the results of the laboratory evaluation.

7.3.2.2 Field Evaluation -

The field evaluation involved determining the monitor's calibration drift and relative accuracy under field conditions. A common ITT-Barton probe/conditioning system was used to extract the flue gas sample from the stack. The extraction system consisted of a probe, a control valve and a vortex condenser. The probe was a thick walled Teflon® tube inside a stainless steel liner.

The gas sample passed from the probe, through the condenser where water is removed, through a heated trace line to a temperature controlled instrument room. Within the instrument room, the sample passed through five impingers in series containing potassium citrate - citric acid buffer solution to remove SO_2 from the gas stream. Leaving the five impingers, the sample gas then passed through a Teflon® filter, a sampling pump and into a common manifold. From the manifold, the sample gas passed to individual analyzers involved in the field evaluation.

Three reference methods were used to determine source gas TRS concentration. The three methods were:

- Federal Reference Method 16;
- Federal Reference Method 16A; and
- NCASI Modified Federal Reference Method 16.

EPA Federal Reference Method 16 for TRS is based on a gas chromatographic separation with subsequent detection of sulfur compounds by flame photometric detection. Federal Reference Method 16A is a wet chemical technique based on SO_2 separation from TRS, oxidation of TRS to SO_2, then capturing the SO_2 in a series of impingers containing hydrogen peroxide. The impingers are analyzed by a barium-thorin titration for sulfates, which are reported as TRS.

NCASI's Modified Method 16 is identical to EPA's Method 16 except that prior to analysis by the gas chromatograph/flame photometric detector (GC/FPD), the gas sample is passed through a thermal oxidizer and the TRS compounds are oxidized to SO_2, just as in Method 16A. The sulfur compounds are then analyzed as SO_2 on the GC/FPD. All other provisions of Method 16 are followed, including removal of source gas SO_2, moisture, and particulate matter prior to analysis. The system was calibrated against a permeation tube calibration device.

The monitors were tested in the field for calibration drift and for relative accuracy. Calibration drift is determined by comparing monitor response to zero and span test gases.

TABLE 7.3
NCASI EVALUATION OF TRS DETECTORS - STUDY #2
LABORATORY EVALUATION

Manufacturer	Detection Principle	TRS Analyzed As	Operating and Maintenance Experience	Converter Study		Interference Study	
				Oxidizing Potential	Modifications	NO Gas	CO_2 Gas
Candel Dynalyzer Series 300 Portable TRS Analyzer P.O. Box 2580 Sidney, British Columbia	Electro-chemical	SO_2	o slow response o difficult to calibrate due to sensitivity of zero/span potentiometers. o confusing dial settings	Complete oxidation of TRS compounds	None	+5%	None
ITT - Barton Model 411 TRS Monitor P.O. Box 1882 City of Industry, CA	Coulometric Titrator	SO_2	o occasional flow rate adjustments o failure of silicone tubing o cell reach equilibrium (30 min) after changing ranges.	Not able to oxidize all TRS compounds	Additional insulation with quartz wool	None	None
Monitor Labs Model 8850 SO_2 Analyzer	Fluorescent	SO_2	No major problems	Not able to oxidize all TRS compounds	Use of another oxidizer during field evaluation.	±1%	None
STI Model 100 TRS Monitor P.O. Box B Waldron, AR	Fluorescent	SO_2	No major problems	Complete oxidation of TRS compounds	None	+0.5%	None
Theta Sensors Portable TRS Monitor 17635A Rowland Street La Puente, CA	Electro-chemical	SO_2	-	Oxidizer not supplied by manufacturer	-	Not tested	Not tested
Tracor Atlas Model 856/825 TRS Monitor	Impregnated Lead Acetate	Total Reducible Sulfur (H_2S)	o Flow rate sensitive o Back pressure sensitive o Difficult to calibrate	Non applicable due to measurement technique	-	None	None

Performance Specification Test 5 requires that the detector span must be checked at 90 to 100 percent of the full scale level, and the full scale span level must be between 1.5 times the emission standard (5 ppm for Kraft recovery furnaces) and the maximum span value (30 ppm). The zero calibration must be checked using a test gas containing no TRS or at a level up to 20 percent of the span level. In order for a monitor to satisfy the PS 5 calibration drift criteria, its calibration drift over a 24 hour period must not exceed 5 percent (1.5 ppm) of the span value (30 ppm) for at least 6 out of 7 days.

Performance Specification Test 5 defines relative accuracy (RA) as:

$$RA = \frac{\overline{d_i} + |cc|}{RM} \times 100$$

where:

d_i = (monitor value) - (reference method value);

$\overline{d_i}$ = arithmetic mean of d_i's;

$cc = t_{0.975} \frac{S_d}{n}$;

RM = arithmetic mean of reference methods; and

n = number of tests.

PS 5 specifies that for a CEM to be acceptable, the RA must not exceed either 20 percent of the RM or 10 percent of the standard, whichever is greater.

According to PS 5, the RA test must include a minimum of nine RM tests. Each RM test must be conducted within 30 to 60 minutes. More than nine RM tests may be performed and included in the RA determination. Additionally, if more than nine RM tests are performed, as many as three tests may be excluded from the RA determination, as long as a minimum of nine are included.

Table 7.4 illustrates the results of both the calibration drift test and the relative accuracy test for the evaluated monitors.

7.3.3 Test Results Summary

A total of 47 relative accuracy tests were performed on all monitors. Table 7.5 reflects the number of tests passed for each monitor, while Table 7.6 displays overall performance of the TRS monitors.

Results of the study indicated the ITT Barton Coulometric Titrator and the STI Model 100 TRS monitor produced TRS concentrations representative of the gas chromatographic reference method. Both of these monitoring principles met Performance Specification Test Relative Accuracy criteria (± 20%) in approximately 90% of the tests. The other monitors performed with less accuracy.

TABLE 7.4
NCASI EVALUATION OF TRS DETECTORS - STUDY # 2
LABORATORY/FIELD EVALUATION

Manufacturer	Calibration Drift Results (5% of span value)		Average Relative Accuracy Test (%)[3] Monitor Span			General Comments
	0-5 ppm	27-30ppm	7.5	10	30	
Candel Dynalyzer Series 300 Portable TRS Analyzer P.O. Box 2580 Sidney, British Columbia	Passed[1]	Failed[1]	F 125	F 151	F 67	o Analyzer tested designed for much higher concentrations; o Positive interference from NO (+5%).
ITT - Barton Model 411 TRS Monitor P.O. Box 1882 City of Industry, CA	Passed[2]	Passed[2]	13	14	12	o Cell temperature/TRS content of stack gas affects life of monitor; o Replacement of cell once per month.
Monitor Labs Model 8850 SO_2 Analyzer	Passed[2]	Passed[2]	13	22	18	o Limited life of hydrocarbon cutter (~3 weeks); o Response to calibration gases in oxygen different than calibration gases in nitrogen.
STI Model 100 TRS P.O. Box B Waldron, AR	Passed[2]	Failed[2] (3rd test)	11	13	13	o No rotameter to indicate calibration gas flowrate.
Theta Sensors Portable TRS Monitor 17635A Rowland Street La Puente, CA	Passed[1]	Failed[1]	126	-	360	o Original monitor sold as source level SO_2 analyzer, 0-100 ppm. Manufacturer changed electronics, but instrument became inoperative after 4 months of testing; o Electrochemical sensor poisoned by reduced sulfur gases.
Tracor Atlas Model 856/825 TRS Monitor	No test performed	No test performed	-	34	26	o Replacement of lead acetate tape and acetic acid blubber every two weeks; o Because monitor cycles, difficult/time consuming to zero/span instrument; o Condensed moisture problem associated with back pressure vent.

[1] Summary of two tests
(P= Pass; F= Fail)
[2] Summary of three tests
[3] Relative Accuracy Criteria (± 20%);
[4] Nine samples per test at each monitor span value.

TABLE 7.5
NCASI RELATIVE ACCURACY TEST PASSED

Manufacturer	Number of Relative Accuracy Tests Passed[1]	Total Relative Accuracy Tests Performed
Candel	4	47
ITT Barton	34	47
Monitor Labs	20	45
STI	35	44
Theta Sensors	0	26
Tracor Atlas	2	10

[1] Criteria: ± 20% Relative Accuracy

TABLE 7.6
RELATIVE ACCURACY TEST RESULTS - FRACTION OF RELATIVE ACCURACY TESTS PASSED

Instrument	9/9 Runs	9/12 Runs
ITT-Barton	14/21 (67%)	18/21 (86%)
Candel Analyzer	0	0
Carlton Technology Monitor Lines	7/21 (33%)	13/21 (62%)
STI	18/21 (86%)	21/21 (100%)
Theta Sensors	0	0
Tracor Atlas	withdrawn	withdrawn

8.0 THE REFERENCE METHOD

8.1 INTRODUCTION

Federal Reference Method 16, Semicontinuous Determination of Sulfur Emissions from Stationary Sources, was promulgated February 23, 1978. The method utilizes the principle of gas chromatography (GC) separation of sulfur species with subsequent flame photometric detection (FPD). Figure 8.1 illustrates the basic components of Federal Reference Method 16 analytical configuration.

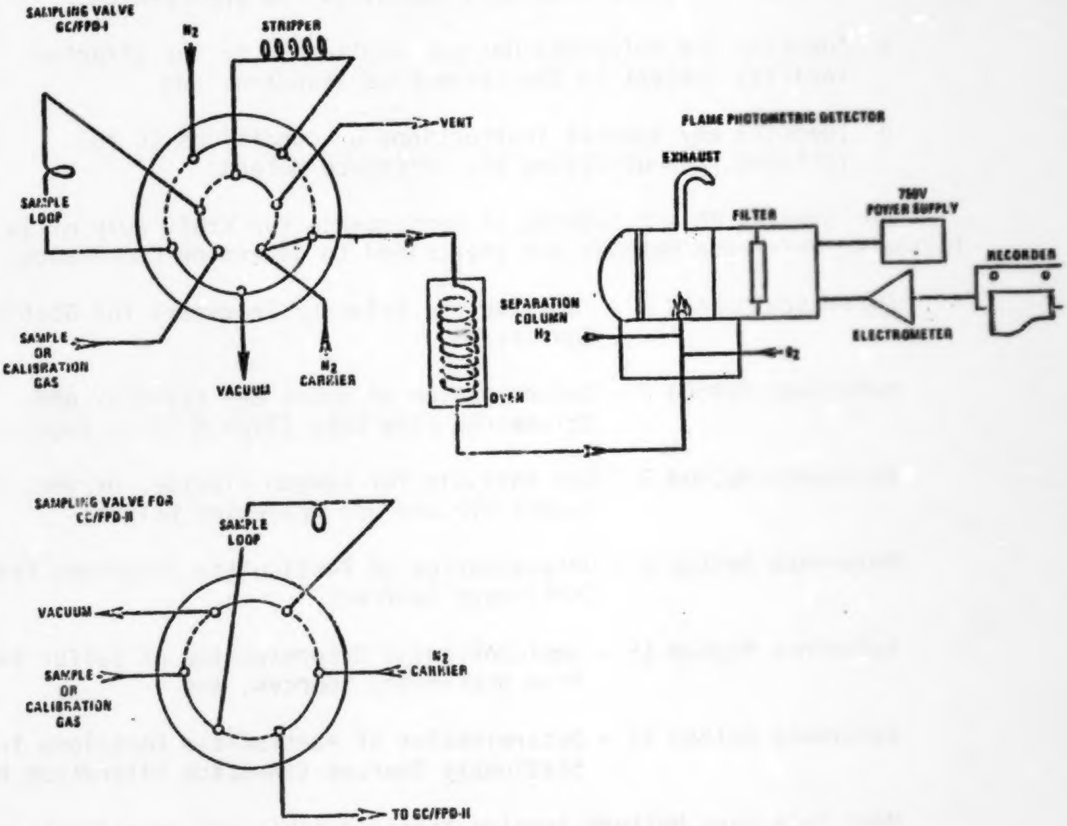

SAMPLING VALVE GC/FPD-I
N_2
STRIPPER
VENT
SAMPLE LOOP
SAMPLE OR CALIBRATION GAS
VACUUM
N_2 CARRIER
SEPARATION COLUMN H_2
OVEN
FLAME PHOTOMETRIC DETECTOR
EXHAUST
FILTER
750V POWER SUPPLY
RECORDER
ELECTROMETER
H_2
SAMPLING VALVE FOR GC/FPD-II
SAMPLE LOOP
VACUUM
SAMPLE OR CALIBRATION GAS
N_2 CARRIER
TO GC/FPD-II

Figure 8.1. Federal Reference Method 16 Analytical Configuration.

As defined in Subpart A - General Provisions, of 40 CFR 60, a "Reference Method" means any method of sampling and analyzing for an air pollutant as described in Appendix A - Reference Methods. The Reference Methods are promulgated by EPA to provide uniform analytical methods to ensure consistency and accuracy in the data generated. The legal authority for this action lies in Sections 111, 114 and 301 (a) of the Clean Air Act. In brief, it states:

> "...within 120 days after the inclusion of a category of stationary sources in a list under subparagraph (A), the administrator shall publish proposed regulations, establishing Federal Standards of Performance for new sources within such category."

The prescribed Reference Method to be used to determine compliance with a standard is specified in the subparts associated with the affected facility as part of the standard of performance. Within each Subpart, a section titled: "Test Methods and Procedures" is provided to:

- Identify the Reference Methods applicable to the affected facility subject to the respective standard; and
- Identify any special instructions or conditions to be followed when utilizing the Reference Method.

For Subpart BB - Standards of Performance for Kraft pulp mills, the following Reference Methods are prescribed to determine compliance:

Reference Method 1 - Sampling and Velocity Traverses for Stationary Sources;

Reference Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube);

Reference Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air and Dry Molecular Weight;

Reference Method 5 - Determination of Particulate Emissions from Stationary Sources;

Reference Method 16 - Semicontinuous Determination of Sulfur Emissions from Stationary Sources; and

Reference Method 17 - Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method).

Most Reference Methods involve specific equipment specifications and procedures, and only a few methods rely on performance criteria. Reference Method 16 is one of the exceptions to the rule. Reference Method 16 has established criteria by which any system design can be used as long as it meets this criteria. Consequently, certain specific equipment or procedures are recognized in the method as being acceptable or "potentially" acceptable. Those items identified in the method as acceptable options may be used without approval from EPA. The potentially approvable options are cited as "subject to the approval of the Administrator."

8.2 FEDERAL REFERENCE METHOD 16

Federal Reference Method 16, as promulgated in the Federal Register, Thursday, February 23, 1978, is divided into thirteen (13) sections. Figure 8.2 outlines those sections.

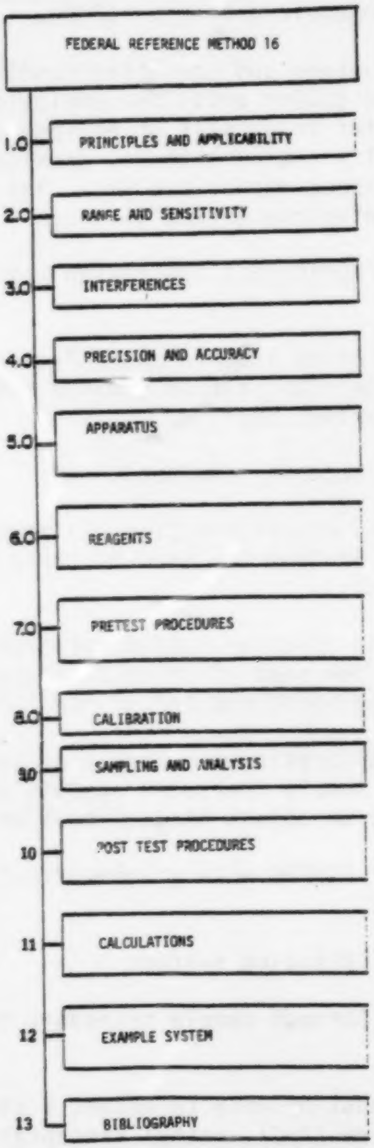

FEDERAL REFERENCE METHOD 16
1.0 PRINCIPLES AND APPLICABILITY
2.0 RANGE AND SENSITIVITY
3.0 INTERFERENCES
4.0 PRECISION AND ACCURACY
5.0 APPARATUS
6.0 REAGENTS
7.0 PRETEST PROCEDURES
8.0 CALIBRATION
9.0 SAMPLING AND ANALYSIS
10 POST TEST PROCEDURES
11 CALCULATIONS
12 EXAMPLE SYSTEM
13 BIBLIOGRAPHY

Figure 8.2. Federal Reference Method 16 Sections.

Sections 1-6 address such topics as method application, range and sensitivity, interferences, precision/accuracy, apparatus and reagents. It is within these sections that specific equipment or procedures are recognized as being acceptable or "potentially" acceptable for use as the Reference Method. The basic analytical procedure, as outlined in these sections, is the determination of total reduced sulfur (TRS) emissions from Kraft pulp mills utilizing gas chromatography (GC) separation with subsequent flame photometric detection (FPD).

There are many systems and operating conditions that represent usable methods of determining sulfur emissions employing the above principle. These systems may differ in details of equipment and operation; however, they may be used as alternative methods, provided that the criteria established by the reference method are met. The basic criteria for TRS analysis by Federal Reference Method 16 are:

- Gas chromatographic (GC) separation with flame photometric detection (FPD);
- Demonstration of no interferences from moisture condensation, carbon monoxide (CO), carbon dioxide (CO_2), particulate matter and sulfur dioxide (SO_2);
- Precision and accuracy evaluation of:
    - GC/FPD and dilution system calibration precision not to exceed ± 5% from the mean of three known calibration gas injections;
    - GC/FPD and dilution system calibration drift not to exceed 10% from the mean of three known calibration injections made at the beginning and end of any 8-hour period; and
    - system calibration accuracy must be determined, through the complete sample transport system, and a correction factor developed to adjust the calibration accuracy to 100 percent.
- Calibration of GC/FPD with gravimetrically calibrated and certified permeation tubes;
- Calibration of dilution system;
- Losses of H_2S through sample transport system not to exceed 20%; and
- Total system must be able to detect a minimum of 1.0 ppm of hydrogen sulfide (H_2S), methyl mercaptan CH_3SH, dimethyl sulfide $(CH_3)_2S$ and dimethyl disulfide $(CH_3)_2S_2$.

8.2.1 Reference Method 16 Sampling System

Federal Reference Method 16 sample system consists of five basic components:

- probe/SO_2 scrubber system;
- sample line/pump system;
- dilution system;
- analysis system; and
- calibration system.

8.2.1.1 Probe/SO_2 Scrubber System -

The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter (in-stack or out-of-stack) and allow calibration gas to enter at or near the sample entry point.

Since SO_2 interferes with the detection of TRS compounds, it must be removed prior to analysis by the GC/FPD. A series of scrubbers, located as close to the probe as possible, utilizing potassium citrate - citric acid buffer solution should be used to remove SO_2.

8.2.1.2 Sample Line/Pump -

The sample line must be made of Teflon®, no greater than 1.3 cm (1/2in) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120°C. The sample pump shall be a leakless Teflon®-coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120°C.

8.2.1.3 Dilution System -

The dilution system must be constructed such that all sample contacts are made of inert materials (stainless steel or Teflon®). It must be heated to 120°C and be capable of approximately a 9:1 dilution of the sample.

8.2.1.4 Analytical System -

The analytical system involves the gas chromatograph columns and subsequent flame photometric detector. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatograph of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale.

8.2.1.5 Calibration System -

The calibration system involves the permeation tube calibrator system with flow system support and constant temperature bath.

Hermetically sealed FEP Teflon® permeation tubes, one each of H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$, gravimetrically calibrated and certified at a stated temperature, will be used to generate known concentrations of pollutant atmospheres to calibrate the GC/FPD system. The permeation tubes will be placed in the constant temperature bath 24 hours prior to use to allow for stable flow and tube equilibrium to be reached. When the temperature is constant, the calibration gases will permeate through the tube wall and mix with the diluent flow passing over the tubes. The total flow should be accurately measured for final concentration determination.

The diluent air should contain less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

8.2.1.5.1 Flow System -

The flow system should be able to measure gas flow within ±2 percent. Each flow measuring device should be calibrated after a complete series of tests with a wet test meter.

8.2.1.5.2 Constant Temperature Bath -

A constant temperature bath is required to maintain the permeation tubes at the calibration temperature within ±0.1°C.

Once the complete system is assembled, verification of system integrity is determined by:

- leak check procedures;
- calibration of analyzer system;
- calibration of dilution system; and
- system performance check.

These checks are covered in Sections 7.0, 8.0, 9.0 and 10.0 of the Reference Method. In essence, these sections cover the sequence of test procedures used during the compliance test.

8.2.2 Sample Extraction

8.2.2.1 Pretest Procedures (Section 7.0) -

The pretest procedures are optional; however, the regulations strongly suggest that they be incorporated into a test protocol. The pretest procedures involve:

- positive/negative leak check of the sampling train; and
- determining system performance.

The positive leak check is performed by attaching a vacuum gauge to the probe tip, turning on the pump and pulling a vacuum of approximately 2 inches. Once the appropriate vacuum is reached, the pump is turned off and leak rate observed as indicated by the vacuum guage. For components after the pump, a slight positive pressure is applied to the system and leaks are observed with the aid of a liquid solution.

System performance is verified by observing and comparing all flow meters, monitor response to changes in flow rates and other active components of the monitoring system to baseline data.

8.2.2.2 - Calibration of Sampling Train (Section 8.0) -

Section 8.0, Calibration, deals with the preparation and validation of the calibration curve as observed by the detector and the calibration of the dilution system. To accomplish both of these evaluations, a permeation tube system is used to generate known concentrations of H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. A typical permeation tube system used in the field is shown in Figure 8.3.

The permeation tubes for the four reduced sulfur compounds are placed in the constant temperature bath 24 hours prior to usage to allow the tubes to equilibrate. Concentration, ppm, generated by the tubes of the reduced sulfur compounds can be calculated by the following equation:

$$C = K\left[\frac{Pr}{ML}\right]$$

Where:

C = concentration of pollutant produced in ppm;

Pr = permeation rate of tube in μg/min;

M = molecular weight of pollutant (g/g-mole);

L = flow rate,ml/min, of air over the tubes; and

K = gas constant at 20°C and 760 mm.

Consequently, three important variables must be observed and certified in order to ensure the production of a known pollutant. They are:

- Certification of permeation tube emission rate;
- Certification of permeation device temperature; and
- Certification of flowmeters in the calibration system.

Certificates are usually provided by the manufacturer ($\pm$2% of permeation rate) for each permeation tube. The tubes are gravimetrically certified by the vendor, as illustrated in Figure 8.4.

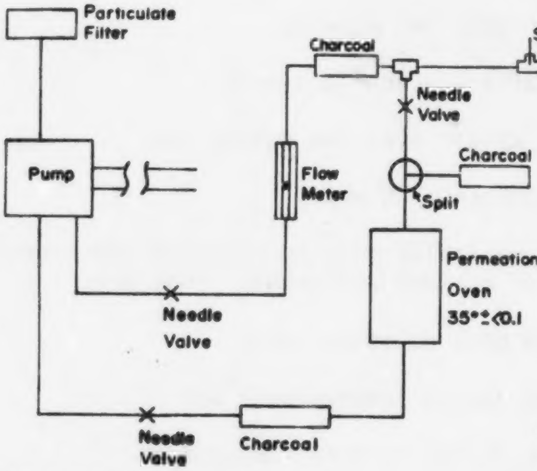
As illustrated in Figure 8.4, the tubes are certified at a specific temperature. The reviewer should verify the calibration of the temperature indicating device.

Certification of flowmeters used in the calibration system should be verified by calibration curves or measured each time by a soap bubble flow tube and a stopwatch.

The calibration system is used to generate a series of three or more known concentrations, spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm), for each of the four reduced sulfur compounds. These test atmospheres are used to check the analyzer system at point A and the dilution system at point B, as illustrated in Figure 8.5.

PORTABLE CALIBRATION SYSTEM
MODEL 320
PERMEATION CHAMBER
FLOW SELECT
ZERO AIR
HIGH CONC
LOW CONC
DILUTION AIR
ADJUST
POWER
OFF
ON
ANALYTICAL INSTRUMENT DEVELOPMENT INC

(a) Commercially Available Portable Permeation Calibration System.

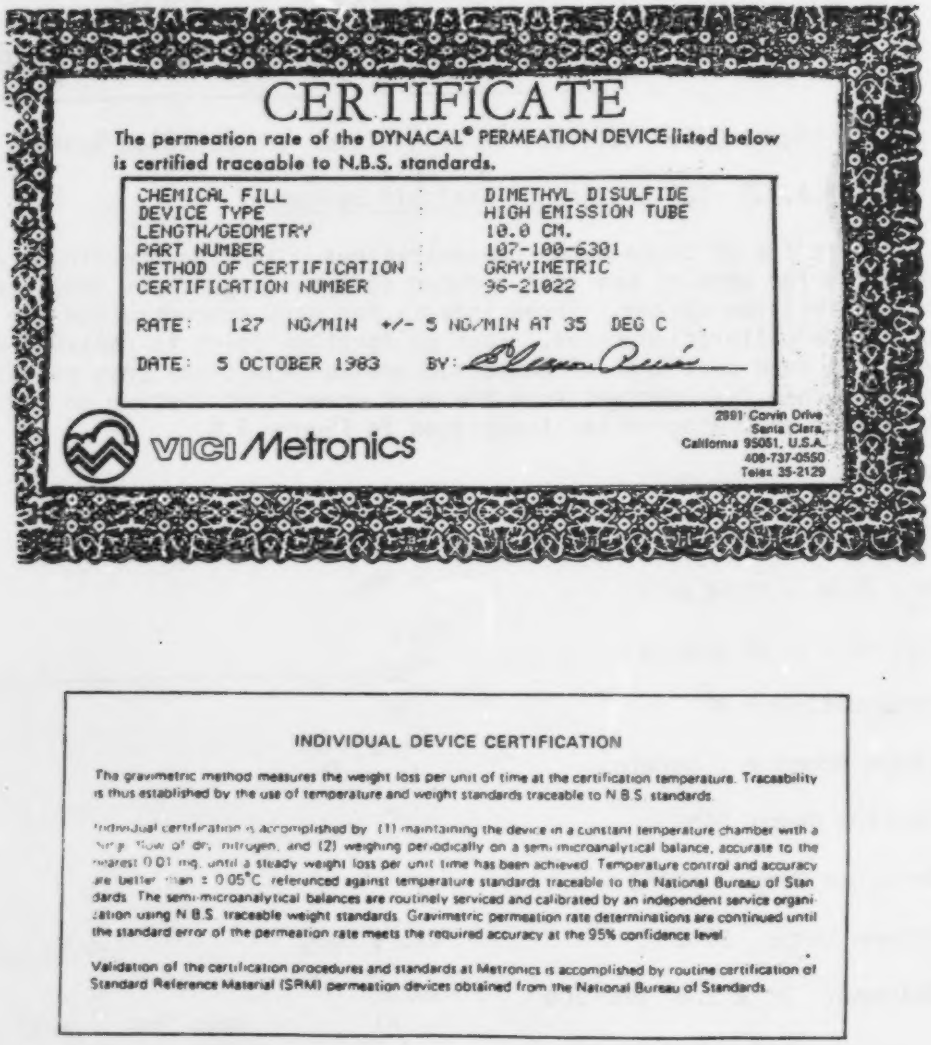

Particulate Filter
Charcoal
Sample
Vent
Needle Valve
Pump
Flow Meter
Charcoal
Split
Permeation
Oven
35°±<0.1
Needle Valve
Needle Valve
Charcoal

(b) Flow Schematic of Portable Calibration System

Reproduced from best available copy.

(c) Permeation Tube Chamber

Figure 8.3. Typical Permeation Tube System.



CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.B.S. standards.

CHEMICAL FILL : DIMETHYL DISULFIDE
DEVICE TYPE : HIGH EMISSION TUBE
LENGTH/GEOMETRY : 10.0 CM.
PART NUMBER : 107-100-6301
METHOD OF CERTIFICATION : GRAVIMETRIC
CERTIFICATION NUMBER : 96-21022

RATE: 127 NG/MIN +/- 5 NG/MIN AT 35 DEG C

DATE: 5 OCTOBER 1983 BY:

VICI Metronics

2991 Corvin Drive
Santa Clara,
California 95051, U.S.A.
408-737-0550
Telex 35-2129

INDIVIDUAL DEVICE CERTIFICATION

The gravimetric method measures the weight loss per unit of time at the certification temperature. Traceability is thus established by the use of temperature and weight standards traceable to N.B.S. standards.

Individual certification is accomplished by (1) maintaining the device in a constant temperature chamber with a slow flow of dry nitrogen, and (2) weighing periodically on a semi-microanalytical balance, accurate to the nearest 0.01 mg, until a steady weight loss per unit time has been achieved. Temperature control and accuracy are better than ± 0.05°C referenced against temperature standards traceable to the National Bureau of Standards. The semi-microanalytical balances are routinely serviced and calibrated by an independent service organization using N.B.S. traceable weight standards. Gravimetric permeation rate determinations are continued until the standard error of the permeation rate meets the required accuracy at the 95% confidence level.

Validation of the certification procedures and standards at Metronics is accomplished by routine certification of Standard Reference Material (SRM) permeation devices obtained from the National Bureau of Standards.

Figure 8.4. Certification of Permeation Tubes.

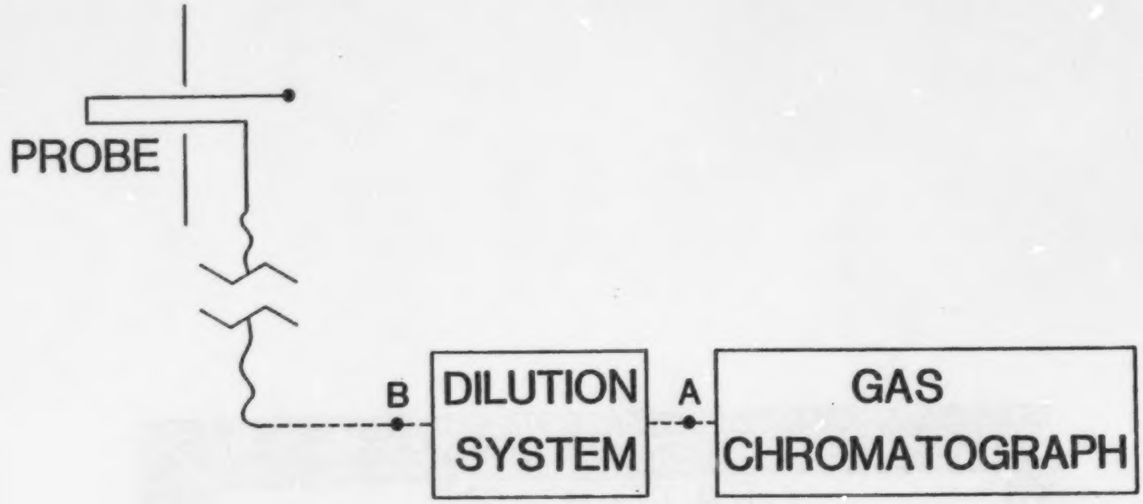


Figure 8.5. Calibration of Analyzer and Dilution System.

8.2.2.2.1 Calibration of Analysis System -

A series of three known concentrations, spanning the linear range of the FPD, for each of the four reduced sulfur compounds is generated by the calibration system. Three injects for each concentration are used to develop a calibration curve. Each calibration point is considered valid when the mean peak area of three successive injections does not differ by more than five percent from the peak areas contributing to the mean. A typical chromatogram is illustrated in Figure 8.6.

H_2 Flow = 50 mL/min

Air Flow = 110 mL/min

$N_2$1 Flow = 25 mL/min

$N_2$2 Flow = 45 mL/min

Attenuation = 2^5

Chart Speed = 1 cm/min

Trailer Temp: 26°C

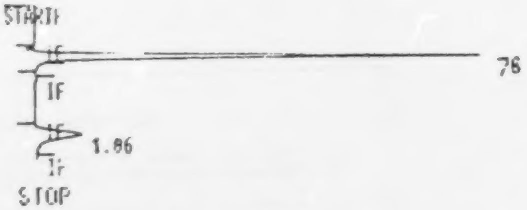
Detector Temp: 115°C

Column Temp: 50°C

Columns: 7' x 1/8" BHT 100
18" x 1/8" PPE

Event 1: 01 sec, Start, Inject

Event 2: 180 sec, Load



```
RUN #  275                    SEP/03/83  14:22:00

AREA%
  RT           AREA TYPE   AR/HT          AREA%
  0.70       695270   PB   0.050         78.269
  1.86       193040   BB   0.133         21.731

TOTAL AREA=      888310
MUL FACTOR= 1.0000E+00
```

Figure 8.6. Typical GC Chromatogram.

The peak area from each injection is measured either manually from the strip chart or electronically through an electronic integrator. The concentration of sulfur in the gas is proportional to the peak area as well as peak height. From this information a calibration curve can be generated, as illustrated in Figure 8.7.

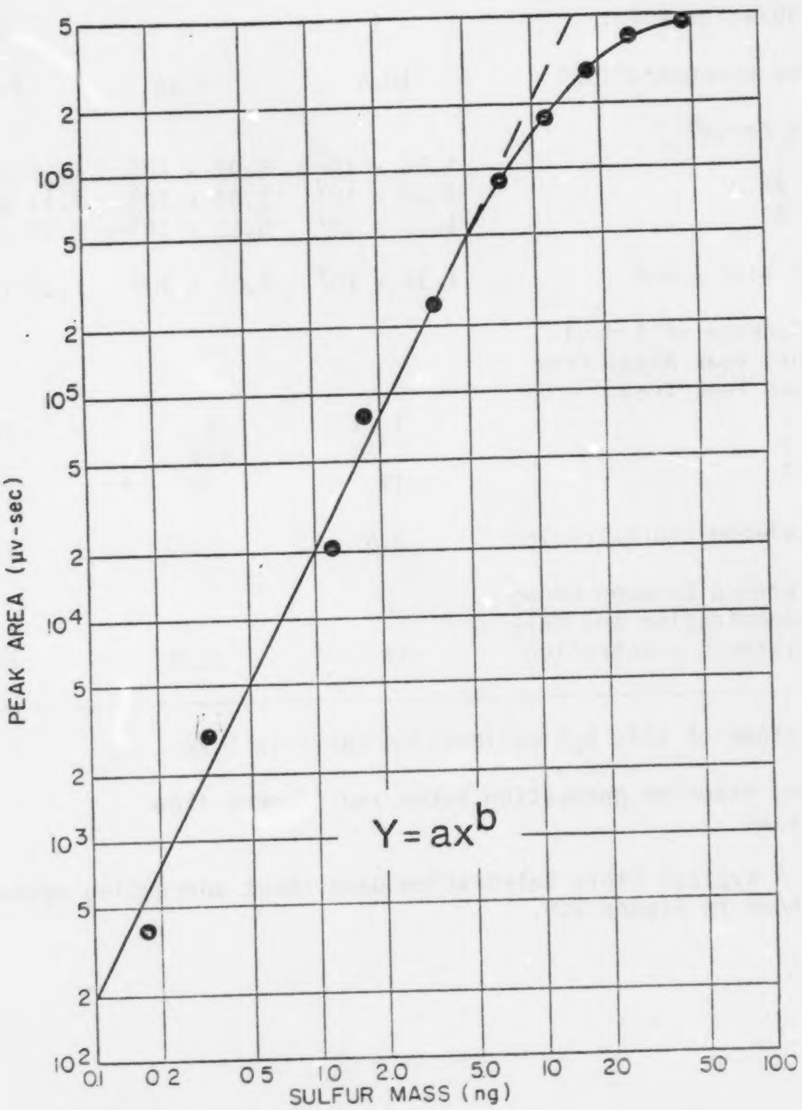


Figure 8.7. Gas Chromatography Calibration Curve.

Table 8.1 displays an example calculation addressing the 5% stipulation associated with repeated injections.

TABLE 8.1

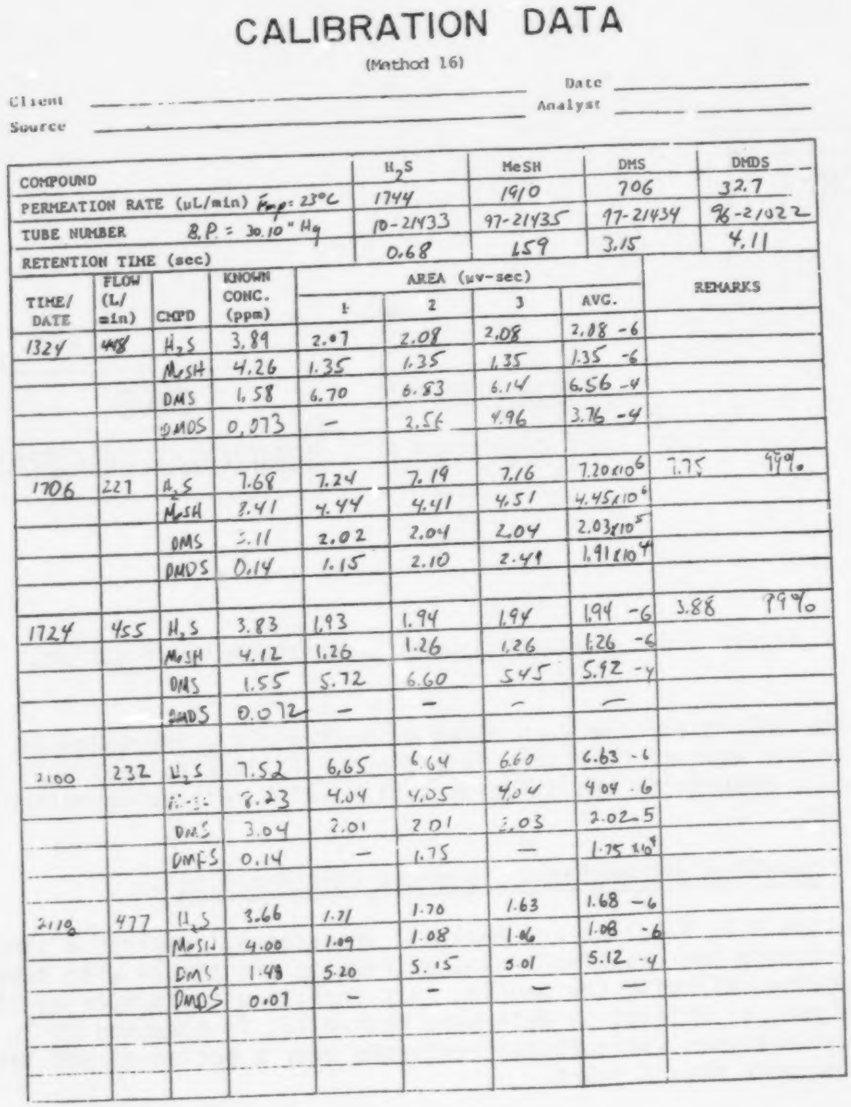
EXAMPLE CALCULATION

Calibration Point	1	2	3	4
Known Concentration[a]	10.5	6.41	2.92	1.39
Peak Areas[b]				
1	1.36×10^7	5.08×10^6	1.19×10^6	3.01×10^5
2	1.32×10^7	5.04×10^6	1.17×10^6	3.13×10^5
3	1.33×10^7	5.11×10^6	1.19×10^6	3.08×10^5
Mean Peak Area[b]	1.34×10^7	5.08×10^6	1.18×10^6	3.07×10^5
Difference of Individual Peak Areas From Mean Peak Area				
1	1.5%	0	<1%	2%
2	1.5%	<1%	<1%	2%
3	<1%	<1%	<1%	<1%
Calculated Concentration	10.6	6.33	2.89	1.40
Difference Between Known Concentration and Calculated Concentration	<1%	1.2%	1%	<1%

The slope of this H_2S calibration curve is 1.86

[a] ppm, based on permeation rates and diluent flow
[b] v-sec

A typical Field Calibration Data sheet addressing system calibration is shown in Figure 8.8.



CALIBRATION DATA

(Method 16)

Client ________________ Date ________________
Source ________________ Analyst ________________

COMPOUND	H_2S	MeSH	DMS	DMDS
PERMEATION RATE (μL/min) Tmp: 23°C	1744	1910	706	32.7
TUBE NUMBER B.P. = 30.10" Hg	10-21433	97-21435	97-21434	96-21022
RETENTION TIME (sec)	0.68	159	3.15	4.11

TIME/ DATE	FLOW (L/min)	CMPD	KNOWN CONC. (ppm)	AREA (μv-sec)				REMARKS
				1	2	3	AVG.	
1324	448	H_2S	3.89	2.07	2.08	2.08	2.08 -6	
		MeSH	4.26	1.35	1.35	1.35	1.35 -6	
		DMS	1.58	6.70	6.83	6.14	6.56 -4	
		DMDS	0.073	–	2.56	4.96	3.76 -4	
1706	221	H_2S	7.68	7.24	7.19	7.16	7.20×10^6	7.75 99%
		MeSH	8.41	4.44	4.41	4.51	4.45×10^6	
		DMS	3.11	2.02	2.04	2.04	2.03×10^5	
		DMDS	0.14	1.15	2.10	2.49	1.91×10^4	
1724	455	H_2S	3.83	1.93	1.94	1.94	1.94 -6	3.88 99%
		MeSH	4.12	1.26	1.26	1.26	1.26 -6	
		DMS	1.55	5.72	6.60	5.45	5.92 -4	
		DMDS	0.072	–	–	–	–	
2100	232	H_2S	7.52	6.65	6.64	6.60	6.63 -6	
		MeSH	8.23	4.04	4.05	4.04	4.04 -6	
		DMS	3.04	2.01	2.01	2.03	2.02 -5	
		DMFS	0.14	–	1.75	–	1.75×10^4	
2110	477	H_2S	3.66	1.71	1.70	1.63	1.68 -6	
		MeSH	4.00	1.09	1.08	1.06	1.08 -6	
		DMS	1.48	5.20	5.15	5.01	5.12 -4	
		DMDS	0.07	–	–	–	–	

Figure 8.8. Gas Chromatography Field Calibration Data Sheet.

8.2.2.2.2 Dilution System Calibration -

Using the permeation tube calibrator, a known concentration of H_2S is injected in front of the dilution system (Point B), as illustrated in Figure 8.9, to verify its precision at each dilution stage.

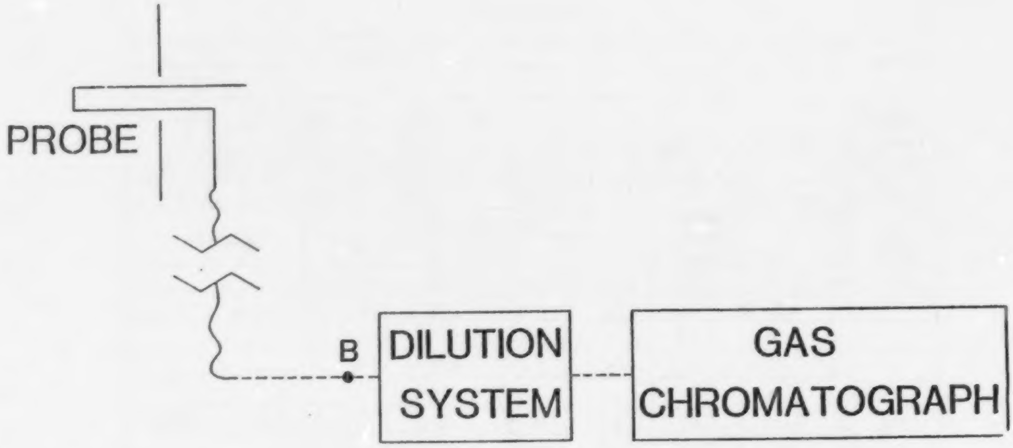


Figure 8.9. Dilution System Calibration Verification.

Three injections for each dilution must yield a precision of ±5 percent from the mean of the three injections. Failure to meet this criteria indicates a problem in the dilution system which must be corrected before proceeding.

8.2.2.3 Sampling and Analysis Procedure (Section 9.0) -

Section 9.0, Sampling and Analysis Procedures, involves a sample run of conditioning the sampling train, extracting the sample with subsequent SO_2 scrubbing, diluting the sample, then analyzing the sample by the GC/FPD. A sample run, as defined by Reference Method 16, is composed of 16 individual analyses (injections) performed over a period of not less than 3 hours or more than 6 hours.

8.2.3 Post-test Procedures (Section 10.0)

Section 10.0, Post-test Procedures, involve determining H_2S losses through the sample transport system to develop a "correction factor" if the sampling losses are between 0-20 percent. For sampling losses greater than 20 percent in a sample run, the sample run is not to be used when determining the arithmetic mean of the performance test.

Sample line losses determination involves injecting a known concentration of H_2S [at a level of the applicable standard ($\pm 20\%$)], as close to the probe tip (Point C) as applicable, as illustrated in Figure 8.10.

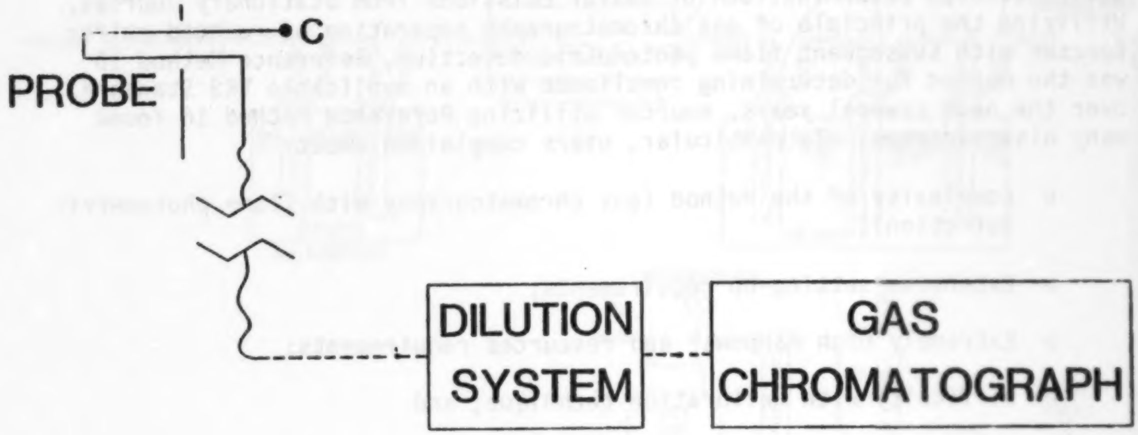


Figure 8.10. Sample Line Loss Determination.

The sample must go through all active components of the sampling system. The H_2S concentration may be generated either by a permeation tube system or by a cylinder gas dilution system which is traceable to a permeation tube system.

The sample line recovery determination is calculated by the following equation:

$$\%\ \text{Recovery} = \frac{(\text{Measured } H_2S\text{, ppm})}{(\text{Known } H_2S\text{, ppm})} \times 100$$

In addition to determining % recovery of the sampling train, a recalibration of the dilution system and the GC/FPD is required after a run or series of runs. This involves challenging the dilution system and GC/FPD with a known concentration of H_2S, generated either by the permeation tube system or by the cylinder gas dilution system.

The calibration curve obtained prior to the run(s) is compared with the recalibration curve. A calibration drift is then calculated by the following equation:

$$\begin{array}{l}\text{Post calibration drift} \\ \text{determination (\%)}\end{array} = \frac{\left[\begin{array}{c}\text{Monitor Response} \\ \text{to } H_2S\text{, ppm}\end{array}\right] - \left[\begin{array}{c}\text{Known Concentration} \\ \text{of } H_2S\text{, ppm}\end{array}\right]}{[\text{Known Conc. of } H_2S\text{, ppm}]} 100$$

The recalibration drift for the dilution system and the GC/FPD should not exceed ± 10%. If the drift exceeds the limits, the intervening run or runs should be considered not valid.

8.3 PROPOSED FEDERAL REFERENCE METHOD 16A - June 18, 1981

8.3.1 Introduction

On February 23, 1978, EPA promulgated Federal Reference Method 16 - Semicontinuous Determinatiuon of Sulfur Emissions from Stationary Sources. Utilizing the principle of gas chromatography separation of reduced sulfur species with subsequent flame photometric detection, Reference Method 16 was the method for determining compliance with an applicable TRS Standard. Over the next several years, sources utilizing Reference Method 16 found many disadvantages. In particular, users complained about:

- Complexity of the Method (gas chromatography with flame photometric detection);
- Extensive setting-up requirements;
- Extremely high manpower and resources requirements;
- Difficulty with calibration technique; and
- Need for maintaining an extensive calibration system.

On June 18, 1981, EPA Proposed Reference Method 16A for determination of total reduced sulfur (TRS) emissions from stationary sources. Different from Reference Method 16, Proposed Reference Method 16A involves sample extracting through an impinger train similar to Federal Reference Method 6. Once the TRS as SO_2 is captured in the Proposed Reference Method 16A impingers, analysis is by barium-thorin titration. Proposed Reference Method 16A advantages over Method 16 are:

- Cheaper testing equipment;
- Easier application of methodology;
- Fewer manpower and resource requirements; and
- Easier sample analysis and calibration.

8.3.2 Train Configuration

As illustrated in Figure 8.11, Proposed Reference Method 16A sampling train involves four basic components:

- sample extraction system;
- sample conditioning;
- impinger system; and
- meter box assembly.

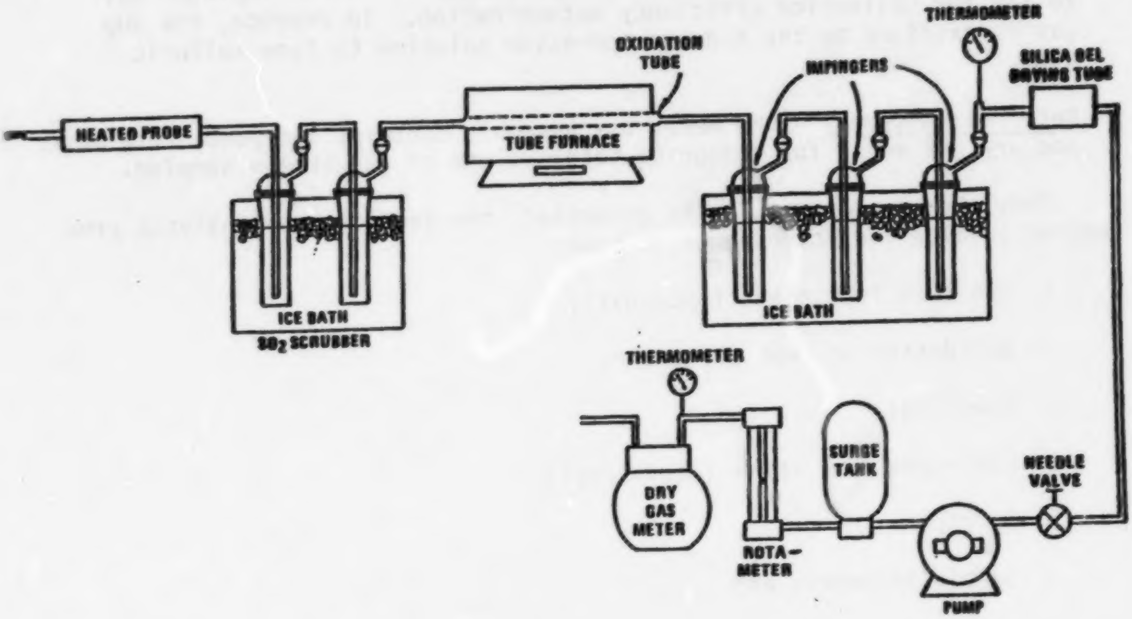

THERMOMETER
OXIDATION TUBE
IMPINGERS
SILICA GEL DRYING TUBE
HEATED PROBE
TUBE FURNACE
ICE BATH
SO_2 SCRUBBER
ICE BATH
THERMOMETER
SURGE TANK
NEEDLE VALVE
DRY GAS METER
ROTA-METER
PUMP

Figure 8.11. Proposed Federal Reference Method 16A Sample Train Configuration.

- Sample Extraction System - The sampling probe consists of a heated Teflon® tube sheathed in a stainless stell probe. A piece of glass wool plug positioned at the inlet of the probe serves as the particulate control device.

- Sample Conditioning System - The sample conditioning system involves the SO_2 scrubber system and the combustion tube furnace. The SO_2 scrubber system consists of two midget impingers in series (top packed with glass wool to eliminate entrained mist) and charged with potassium citrate-citric acid buffer solution. As the stack gas bubbles through the buffer solution, SO_2 is subsequently removed while TRS passses through.

The combustion furnace consists of a quartz glass tube 30.5 cm long, heated and maintained at 815± 15°C. This enables the oxidation of TRS to SO_2.

- Impinger System - The impinger train consists of three midget impingers, in series, charged with 3% hydrogen peroxide. A fourth impinger may follow for collection efficiency determination. In essence, the SO_2 gas is oxidized by the hydrogen peroxide solution to form sulfuric acid.

- Meter Box Assembly - The meter box assembly contains the pump, rate meter and dry gas meter for measuring total volume of gas stream sampled.

Once the complete system is assembled, the sampling and analysis procedures involve the following functions:

- Pre-test leak check (optional);
- Validation of test procedure;
- Sampling;
- Post-test leak check (mandatory);
- Purging:
- Sample recovery; and
- Sample analysis.

Since its proposal in 1981, the method has shown interferences in sampling and analysis from particles when applied to monitoring lime kiln stack gases. Previous work by EPA has indicated that if particulate matter (calcium carbonate) is allowed to enter the SO_2 scrubber (citrate buffer solution), it would raise its pH, this permitting H_2S to be absorbed prior to oxidation, creating a negative bias in the sampling technology.

8.3.3 Proposed Reference Method 16A Bias Evaluation

EPA evaluated five sampling parameters for biases involving Proposed Reference Method 16A train configuration. They were:

- Probe angle;
- External filter;
- H_2S filter retention;
- Sample train purge; and
- Scrubber solution pH.

Four sampling trains were used to evaluate the above parameters. Each individual train consisted of a heated probe, filtering device, a series of impingers and a meter box console. During sampling, the probe and filter temperatures were maintained at approximately 107°C (225°F). All sampling trains were run for 3 hours at a flow rate of 2 liters per minute (liter/min) to simulate actual Proposed Reference Method 16A lime kiln sampling procedures. The study, in essence, evaluated the front half of the Proposed Reference Method 16A sampling train.

8.3.3.1 Probe Angle Evaluation -

A series of tests were performed to evaluate the use of an angle probe rather than a straight-in probe as recommended in Proposed Method 16A. The test involved four simultaneous sampling trains extracting samples at a lime kiln and evaluating the quantity of particulate matter captured by the sampling train.

Two sampling trains (AP-1 and AP-4) employed angled probes while the other two trains (SP-2 and SP-3) employed straight probes. The results of probe angle evaluation are shown in Table 8.2.

TABLE 8.2
PROBE ANGLE EVALUATION

Test Run	Sampling train configuration	Test time, min.	Average Temperature (°F) Probe	Average Temperature (°F) Filter	Particulate Matter Catch, mg Probe rinse	Particulate Matter Catch, mg Filter	Particulate Matter Catch, mg Total	Total Particulate Matter Catch in Sampling Train, mg/Nm³
1	AP-1	180	95 (203)	116 (241)	4.5	21.2	25.7	76.3
	SP-2	180	109 (229)	121 (250)	1025	60.0	1085	2840.3
	SP-3	180	103 (217)	117 (242)	884	76.9	960.9	2676.6
	AP-4	180	104 (219)	123 (253)	6.2	26.9	33.1	89.9

The results demonstrate a substantial amount of particulate matter is retained by the Proposed Reference Method 16A sampling train utilizing a straight-end probe. If used in this configuration, chances of particle interferences are substantial. The angle probe rejected more particulate than the straight-end probe.

8.3.3.2 External Filter Evaluation -

In a series of tests, EPA evaluated a 50-mm heated Teflon® filter holder with both a micro-pore size membrane and a coarse pore size membrane. A schematic of the filter holder is shown in Figure 8.12.

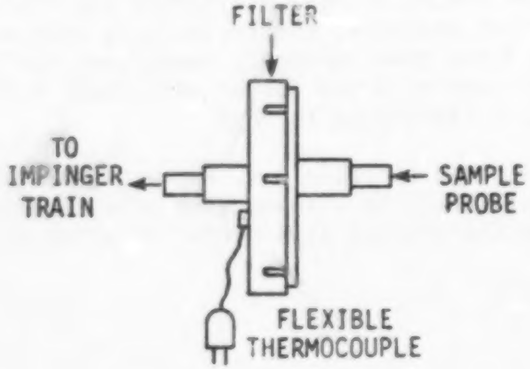


Figure 8.12. 50 mm Heated Teflon® Filter Holder.

The main object of the test series was to evaluate different particulate matter removal devices to improve overall sampling collection efficiency of the Proposed Reference Method 16A train configuration.

The results of the test are indicated in Table 8.3.

TABLE 8.3
EXTERNAL HEATED FILTER EVALUATION

Test Run	Sample No.	Sampling Train Configuration[a]	Test Time, min.	Sample Volume, Nm^3 (dscf)	Particulate Catch, mg			Concentration of Particles in Sampling Train mg/Nm^3
					Probe Rinse	Filter	Total	
2	1	AP-T50M	180	0.340 (12.019)	6.9	17.1	24.0	70.6
	2	AP-T50M	180	0.366 (12.940)	5.7	17.3	23.0	62.8
	3	AP-T40C	180	0.352 (12.449)	8.6	10.9	19.5	55.4
	4	AP-T40C	180	0.341 (12.052)	6.8	16.8	23.6	69.2

AP-T50M = Angled probe, Teflon® 50-mm filter, micro-pore size (1-2 µm)
AP-T50C = Angled probe, Teflon® 50-mm filter, coarse-pore size (20-30 µm)

The micro-pore size filter particulate catch average approximately 66.7mg/Nm^3, slightly more than the coarse-pore filter with an average of 62.3mg/Nm^3.

8.3.3.3 Sampling Train Purge Evaluation -

As specified in Proposed Method 16A, an impinger train of citrate acid buffer solution is used to scrub out interfering SO_2, while allowing H_2S to pass. In this series of tests, EPA evaluated the ability of the scrubber solution to pass H_2S.

A series of two tests, each test composed of four simultaneous sampling trains, involving sampling a known concentration of H_2S gas were conducted. After each test, the impinger trains were purged with clean, dry air before analyzing the amount of H_2S retained in the citrate acid buffer solution. After the first analysis, the trains were further purged for an additional 4 minutes and the same impingers reanalyzed for H_2S. After that analysis, the train were again purged for an additional 4 minutes and the impingers were once again reanalyzed for H_2S.

The results, illustrated in Table 8.4, indicate that a sufficient purge time (>10 minutes) should be allowed when using Proposed Reference Method 16A to condition the citrate acid buffer solution to H_2S source gas concentration.

TABLE 8.4
HYDROGEN SULFIDE RECOVERY CHECK

Sample Train No.	Average H_2S Concentration, ppm[1]	% difference		
		Between first analysis and average[2]	Between second analysis and average[3]	Between third analysis and average[4]
Test 1				
1	3.76	+10.1	+ 2.1	+ 0.3
2	3.76	+12.2	+ 5.0	+ 1.6
3	3.83	+85.1	+26.4	+ 8.4
4	3.81	+59.6	+12.5	+ 2.1
Test 2				
5	3.69	+14.9	+ 4.1	0.0
6	3.39	- 0.2	0.0	0.0
7	3.59	-13.4	- 4.4	- 1.4
8	3.62	- 6.9	- 3.3	- 1.9

[1] As measured by GC-FPD over test period.

[2] Analysis for H_2S performed on scrubber solution after 4 min. of purging with clean, dry air.

[3] Analysis for H_2S performed on scrubber solution after 8 min. of purging with clean, dry air.

[4] Analysis for H_2S performed on scrubber solution after 12 min. of purging with clean, dry air.

8.3.3.4 Scrubber Solution pH Evaluation -

Under the same sampling conditions as performed in the sample train purge evaluation, it was determined that for best train performance, the pH of the citrate buffer solution should be 7.

8.3.3.5 H_2S Filter Retention Check -

A fifth series of tests were performed to evaluate the retention capability of the filter holder to known concentrations of H_2S. If a filter holder is going to operate efficiently, it must allow H_2S gas to pass with very little retention. The results of that study are illustrated in Table 8.5.

TABLE 8.5
SUMMARY OF RESULTS OBTAINED FROM H_2S RECOVERY CHECKS ON BLANK FILTRATION DEVICES

Sample type	Filter code	% loss of H_2S[a,b]	H_2S Flow Rate, ml/min[c]
Glass Fiber Filter, Glass Holder	M5	34.0 to 34.4	150
	M5	19.7 to 23.4	350
	M5	17.8 to 19.2	300
	M5	1.0 to 2.8	2460
90-mm Teflon Filter and Holder	T90F	0.6 to +1.5 (Gain)	100
50-mm Teflon filter and holder	T50M	0.1 to +0.1 (Gain)	100
Entrapment device	ED	0.5 to +1.5 (Gain)	100

[a] At 95% confidence interval.

[b] 100% recovery assumed if interval includes zero.

[c] Milliliters per minute.

The results indicate the percent of H_2S gas loss utilizing the glass filter holder is considerable at low flow rates and low at high flow rates.

8.3.4 Recommended Design Change to Proposed Reference Method 16A

From this series of tests designed to evaluate Proposed Reference Method 16A sampling train configuration, EPA recommends the following design changes and operation in the proposed method:

- Probe modification involving heating (107° - 121°C) and adaption of an upturned sampling nozzle;
- Adding an external 50-mm Teflon® filter with micro (1-2 μm) pore size heated to 107° to 121°C;
- H_2S sampling train recovery check periodically; and
- 10-minute conditioning period for the citrate buffer solution.

8.4 PROMULGATED FEDERAL REFERENCE METHOD 16A - MARCH 8, 1985

8.4.1 Introduction

As discussed earlier, EPA evaluated the proposed Reference Method 16A sampling train for biases. In particular, interferences from particulate calcium carbonate were evaluated. Due to these studies, modifications to proposed Reference Method 16A were incorporated into the promulgated method. They were:

- Addition of a probe nozzle;
- Use of external heated filter;
- Impinger train configuration; and
- Modification of sampling methodology.

On March 8, 1985, EPA incorporated these revisions into the promulgated Federal Reference Method 16A.

8.4.2 Promulgated Train Configuration

Figure 8.13 illustrates the promulgated Reference Method 16A sampling train configuration, while Table 8.6 summarizes those changes between the proposed and promulgated versions.

8.4.3 Sampling Protocol

Sampling protocol is similar to the proposed Reference Method 16A protocol. In essence, the following activities are involved:

- Sample train preparation;
- Pre-test leak check (optional);
- Validation of test procedure;
- Sampling;
- Post-test leak check (mandatory);
- Purging;
- Sample recovery; and
- Sample analysis.

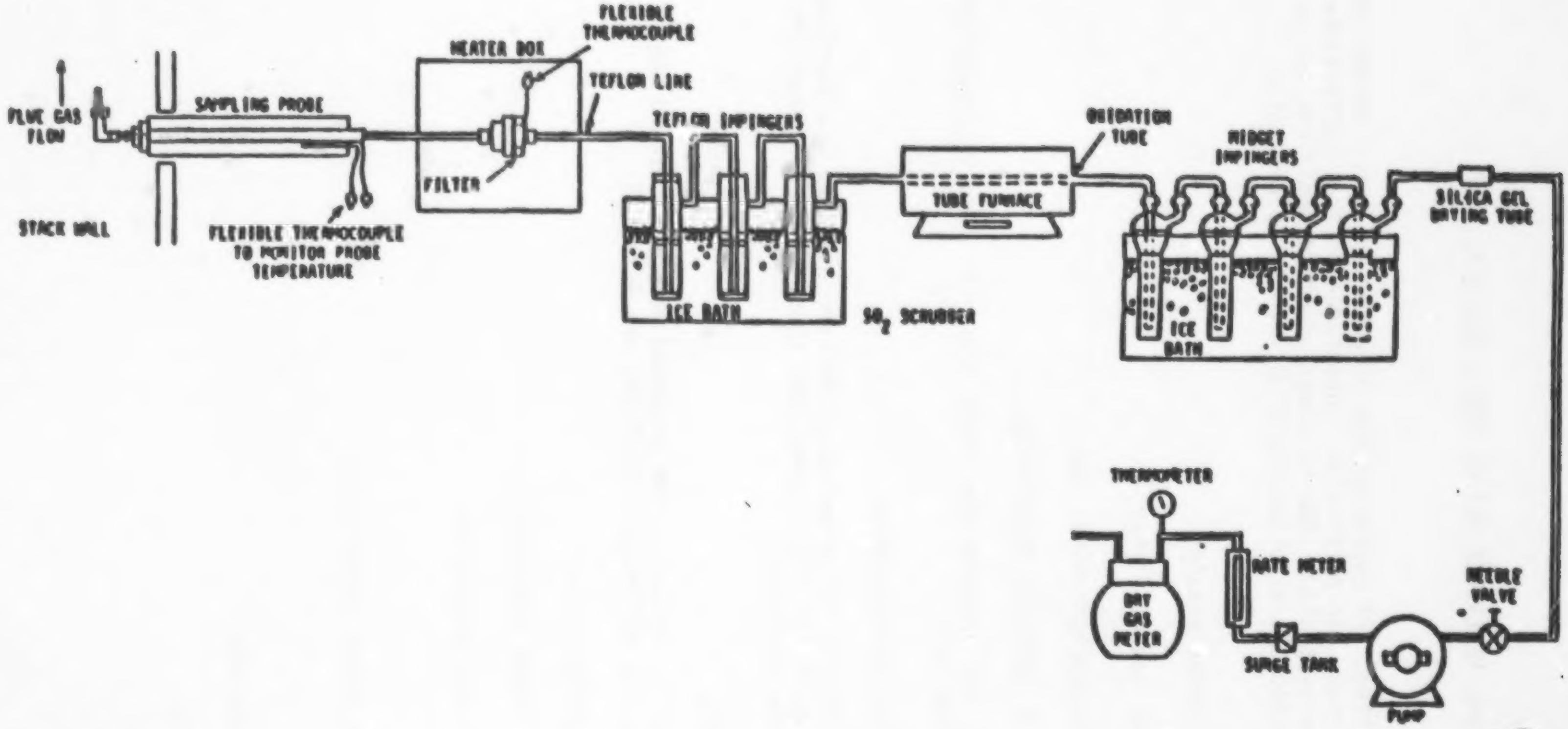

FLUE GAS FLOW
STACK WALL
SAMPLING PROBE
FLEXIBLE THERMOCOUPLE TO MONITOR PROBE TEMPERATURE
HEATER BOX
FLEXIBLE THERMOCOUPLE
FILTER
TEFLON LINE
TEFLON IMPINGERS
ICE BATH
SO_2 SCRUBBER
TUBE FURNACE
OXIDATION TUBE
MIDGET IMPINGERS
ICE BATH
SILICA GEL DRYING TUBE
NEEDLE VALVE
PUMP
SURGE TANK
RATE METER
THERMOMETER
DRY GAS METER

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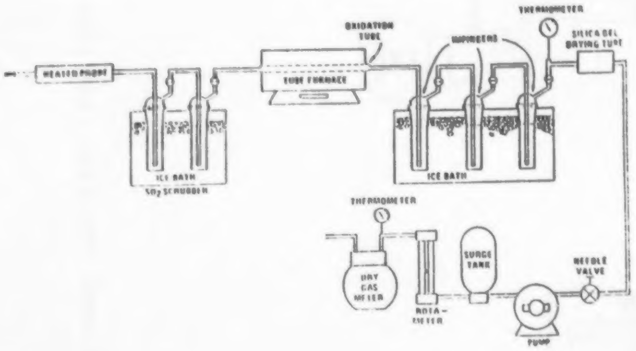
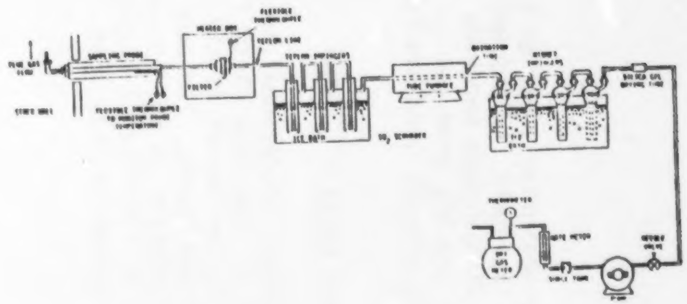
Figure 8.13. Promulgated Federal Reference Method 16A Sampling Train Configuration.

TABLE 8.6
PROPOSED AND PROMULGATED
FEDERAL REFERENCE METHOD 16A

Proposed Reference Method 16A June 18, 1981 (46FR31904)	Promulgated Reference Method 16A March 8, 1985 (50FR9578)
 HEATED PROBE ICE BATH SO_2 SCRUBBER TUBE FURNACE OXIDATION TUBE IMPINGERS THERMOMETER SILICA GEL DRYING TUBE ICE BATH THERMOMETER DRY GAS METER ROTAMETER SURGE TANK NEEDLE VALVE PUMP	
Probe Borosilicate glass or stainless steel; Straight-end, heated, with glass wool plug as particulate control device (in-stack or out-of-stack).	Teflon, heated with upturn elbow.
Particulate Control Device In-stack glass wool plug.	Out-of-stack , 50-mm Teflon filter with micro (1-2 μm) pore size, heated between 107° to 121°C (225°-250°F).
SO_2 Scrubber Two midget impingers in series, top packed with glass wool.	Three 300 ml Teflon impingers. First two impingers contain citrate buffer solution. Third impinger dry.
Furnace Quartz tube (2.54 cm x 30.5 cm), heated at 815± 15°C	Quartz tube (2.54 cm x 30.5 cm), heated at 800°C ± 100°C
SO_2 Absorber Three midget impingers	Three midget impingers
Analysis Barium-thorin titration	Barium-thorin titration

8.4.3.1 Train Preparation

The sample train is prepared by measuring 100ml of citrate buffer solution into each of the first two impingers, (glass wool packed in the top) for SO_2 removal. In addition, 3% hydrogen peroxide is added to the following three impingers to collect the SO_2 produced by the oxidation of TRS. The probe is heated to 106°C to prevent condensation and the oxidizing furnace is maintained at 815°C.

8.4.3.1.1 Optional Pre-test Leak Check -

Once the sampling train is prepared, an optional leak check is recommended. As demonstrated in Figure 8.14, the leak check is performed by attaching a rotameter (0-40 ml/min) to the outlet of the dry gas meter. The probe inlet is plugged with a vacuum gauge. The pump is turned on until a vacuum of 250 mmHg (10"Hg) registers on the vacuum gauge. If the leak rate indicated by the rotameter is less than 2 pecent (40 ml/min) of the average sampling rate, then the system is leak free.

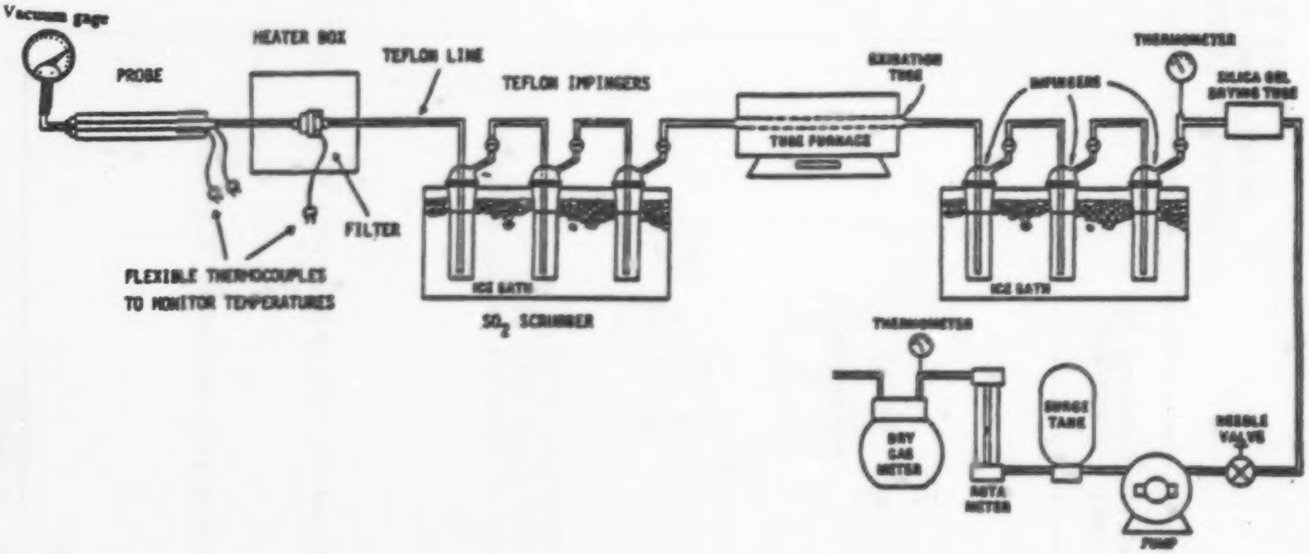

Vacuum gage
PROBE
HEATER BOX
TEFLON LINE
TEFLON IMPINGERS
OXIDATION TUBE
TUBE FURNACE
THERMOMETER
IMPINGERS
SILICA GEL DRYING TUBE
FILTER
FLEXIBLE THERMOCOUPLES TO MONITOR TEMPERATURES
ICE BATH
ICE BATH
SO_2 SCRUBBER
THERMOMETER
DRY GAS METER
ROTA METER
SURGE TANK
NEEDLE VALVE
PUMP

Figure 8.14. Optional Pre-test Leak Check

8.4.3.1.2 System Performance Check -

Once the optional pre-test leak check is performed, a system performance check is required. The objective is to demonstrate that the system can properly oxidize and quantatively recover a known concentration of H_2S. A dilution system is used to generate the known concentration of H_2S, as illustrated in Figure 8.15.

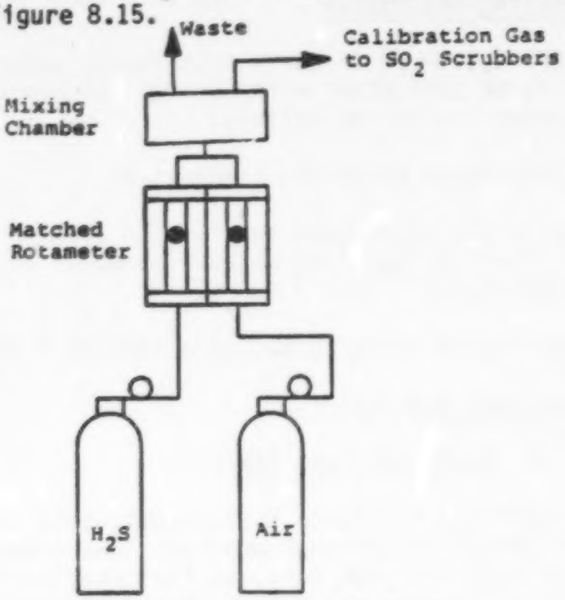


Figure 8.15. Field Dilution System.

This system requires no additional dry gas meter and is very simple to use.

As with any calibration system, quality assurance is important. Two major areas of quality assurance checks should be:

- Certification of gas cylinder used in the dilution system; and
- Certification of flow measuring devices.

The concentration of H_2S gas should be certified by Reference Method 11. The diluent gases should contain no more than 50 ppb of total sulfur compounds and no more than 10 ppm of total hydrocarbons.

Certification of the flow measuring devices should be done against a primary standard. If used in a matched configuration, then temperature and pressure corrections should not apply. (If used in the above configuration, then the flowmeters need not be calibrated if a 1:1 dilution is made.)

Calibrate the flow rate from both sources with a soap bubble flow tube so that the diluted concentration of H_2S can be accurately calculated. Collect 30-minute sample and analyze in the normal manner.

The system performance check specifies that the sampling system is considered acceptable when two samples of calibration gas produce results which do not vary by more than ±5 percent from their mean, and this mean value is within ± 20 percent of the known value.

8.4.3.2 Sampling Activities -

After the system performance test check, actual sampling can be conducted. To be consistent with Federal Reference Method 16, the tester may sample under one of two options:

- Collect three 60-minute samples; or
- Collect one three-hour sample with a total gas sample volume of 120 liters either intermittently (equal samples, equally spaced) or continuously over 3 hours.

Sampling should be performed at a rate of 2 liters/minute (±10%).

8.4.3.3 Post-test Activities

8.4.3.3.1 Post-test Leak Check -

As demonstrated in Figure 8.12, a post-test leak check is performed in a similar manner to optional pre-test leak check. The criteria for acceptance is that the leak rate, as indicated by the rotameter attached to the outlet of the dry gas meter, should be no greater than 2 percent (40 ml/min) of the average sampling rate.

After the mandatory post-test leak check, the sample is recovered from the four impingers containing the hydrogen peroxide and analyzed by barium-thorin titration. The amount of TRS in the original sample is directly proportional to the amount of sulfate formed in the impingers.

8.4.3.3.2 Sample Recovery Test -

After sample recovery and analysis, a sample train recovery test is required. In this test, a known concentration of H_2S is introduced at the probe tip. The obtained concentration should be within ±15 percent of the known value.

8.4.3.3.3 Sample Analysis

After sample, recover the midget impingers content into a single container. Dilute to a known volume. Take a 40-ml aliquot, add 160 ml of 100 percent isopropanol, and four drops of thorin indicator. Titrate from a yellow to a pink endpoint. Analyze an EPA SO_2 field audit sample with each set.

8.4.3.4 Calculations

Calculate the equivalent TRS concentration by the following equation:

$$C_{TRS(ppm)} = K \frac{(V_t - V_{tb})\ N\ (V_{soln} / V_a)}{V_{m(std)}}$$

Where: $C_{TRS(ppm)}$ = Concentration of TRS as SO_2 dry basis corrected to standard conditions, ppm.

V_a = Volume of sample aliquot titrated, ml

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

K = 12025 ul/meq.

N = Normality of standardized $Ba(ClO_4)_2$

Table 8.7 illustrates the performance requirements between the Proposed and Promulgated Reference Method 16A.

TABLE 8.7
SYSTEM PERFORMANCE SPECIFICATION
PROPOSED & PROMULGATED REFERENCE METHOD 16A

Parameter	Proposed Reference Method 16A 6/18/81	Promulgated Reference Method 16A 3/8/85
System Performance Check ($\pm$20% of Calibration gas)	Each Run	2 optional
Citrate Scrubber Conditioning	None	10 min. @ 2 liters/min
Pre-Test Leak Check (<2% of Sampling Rate)	1 (optional)	1 (optional)
Sampling Rate ($\pm$ 10%)	2 liters/min	2 liters/min
Sampling Time	1 hour	1 or 3 hours
Post Test Leak Check (<2% of sampling rate)	1 (mandatory)	1 (mandatory)
Purge	Need not be performed	15 minutes recommended
System Performance Check (after 3 hours) ($\pm$ 20% of calibration gas)	-	1 (mandatory)
EPA Field Audit Sample Analyzed	No	Recommended
Recovery Gas Analysis (5% on three analyses)	-	Yes

8.5 COMPARATIVE TESTING OF METHOD 16 (GAS CHROMATOGRAPHY) AND PROPOSED FR METHOD 16A (WET CHEMICAL)

8.5.1 Introduction

On July 14, 1981, the United States Environmental Protection Agency proposed Federal Reference (FR) Method 16A as an alternative to Federal Reference Method 16. As indicated previously, the disadvantages with FR Method 16 are:

- complexity of Reference Method 16 (gas chromatograph equipped with a flame photometric detector);
- difficulty with calibrating with five sulfur gases;
- need for maintaining an extensive calibration system; and
- expense of Reference Method 16.

Proposed Reference Method 16A was considered cheaper and easier to perform. Utilizing the impinger collection technique and barium-thorin titration procedure, the method offers the following advantages over FR Method 16:

- needed testing equipment is much cheaper;
- method is simpler;
- sampling can be performed on the stack;
- samples need not be analyzed in the field; and
- method has few interferences.

One of the major drawbacks with FR Method 16A is that all reduced sulfur compounds are measured. The method can not distinguish between different reduced sulfur compounds like FR Method 16. When the Kraft pulp mill standard was developed and originally adopted, the intent was to include all reduced sulfur compounds. However, during the emission testing program, EPA found that four compounds- hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide - were the only significant compounds being emitted. Consequently, FR Method 16 addressed only those four compounds through column separation and detection. FR Method 16A, being an impinger technique, collects all reduced sulfur compounds; therefore, FR Method 16A may give higher results than FR Method 16.

8.5.2 Test Configuration

With this in mind, the National Council For Air and Stream Improvement (NCASI) decided to perform a study involved comparing FR Method 16 and Proposed FR Method 16A to H_2S calibration gas mixtures in air and to measuring Kraft recovery furnace TRS emissions. The sampling train configuration involved an ITT Barton probe/conditioning system, a heat trace line, a series of impingers to remove SO_2, and a common manifold for sample distribution.

The ITT Barton probe consists of a Teflon® tube housed inside a stainless steel pipe. The stack gas is extracted from the source through holes in the pipe extending into the stack. The extracted gas sample passes through a condenser, transported by a heated Teflon® sample line to the control room. Inside the control room, the gas stream is scrubbed of SO_2 by five impingers containing potassium citrate - citric acid buffer solution maintained at a pH of 5.5 ± 0.1. The sample then passes a Teflon® manifold where the gas is distributed for concurrent analysis.

Federal Reference Method 16 uses the principle of gas chromatography (GC) separation with flame photometric detection (FPD). A sample is extracted from the source and an aliquot is injected into the gas chromatograph.

The column in the gas chromatograph separates the sample into component fractions, [i.e. hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide $(CH_3)_2S$, and dimethyl disulfide $(CH_3)_2S_2$)] through a gas-solid partitioning mechanism. The column also provides for separation of carbon monoxide (CO) and carbon dioxide (CO_2). The separated components of the gas stream exit the column and are detected by the flame photometric detector. A flame photometric detector measures the emission intensity of a high energy sulfur species at a selected wavelength while the pollutant is burned by a hydrogen-rich flame. The luminescent emission from burning the sulfur molecule in the flame is directly proportional to the sulfur atoms in the gas stream.

The GC/FPD is calibrated against a permeation tube calibration system for the four TRS compounds. The calibration procedure requires three upscale concentrations for each of the four pollutants.

Proposed FR Method 16A utilizes an SO_2 scrubber, TRS oxidation furnace and a series of impingers for absorption. In essence, a gas sample is extracted from a stack, bubbles through a potassium citrate-citric acid buffer solution to remove SO_2, oxidized remaining TRS to SO_2 and captured in a series of impingers containing hydrogen peroxide. The hydrogen peroxide oxidizes the SO_2 to sulfates. The sulfates are titrated by a barium-thorin titration. The amount of sulfates present are directly related to TRS in the sample gas. Calibration of the system is performed by passing certified H_2S in nitrogen gas through the sample train to calculate a percent efficiency.

8.5.3 Test Results

8.5.3.1 H_2S Certified Test Gas Mixture -

Known concentrations of H_2S certified gas mixtures were used to evaluate the response of FR Methods 16 and 16A test configuration. The results from three test runs are presented in Table 8.8.

TABLE 8.8
METHOD COMPARISON: FR METHOD 16 AND PROPOSED FR METHOD 16A UTILIZING H_2S CERTIFIED GAS MIXTURE

Run No.	Avg. Measured TRS Concentration, ppm		Difference, ppm
	FR Method 16	Proposed FR Method 16A	
1	2.09	2.32	-0.23
2	2.10	2.27	-0.17
3	1.85	1.79	+0.06
Avg.	2.01	2.13	-0.11

The results indicate very little difference between the two methods. A paired difference test was performed by NCASI on the data to test whether the difference was significant. Results of that evaluation indicated no significant difference - the two methods essentially provide the same results.

8.5.3.2 Kraft Recovery Furnace Test

FR Methods 16 and Proposed FR Method 16A were compared by analyzing Kraft recovery furnace TRS Emissions. A total of eleven runs were evaluated. Each run for FR Method 16 involves five to six injections equally spaced over an hour. The average of those injections were used to compare to the one hour sampling time for Proposed FR Method 16A. Table 7.8 illustrates the results of the method comparisons analyzing Kraft recovery furnace emissions.

TABLE 8.9
METHOD COMPARISON: FR METHOD 16 AND PROPOSED FR METHOD 16A KRAFT RECOVERY FURNACE

Run #	Measured TRS Concentration, ppm		Difference, ppm
	FR Method 16	Proposed FR Method 16A	
1	2.06	2.32	-0.26
2	3.10	2.61	+0.49
3	5.37	5.40	-0.03
4	3.27	3.11	+0.16
5	1.65	2.18	-0.53
6	1.94	1.98	-0.04
7	0.65	0.88	-0.23
8	2.38	2.68	-0.30
9	2.74	2.85	-0.11
10	2.31	2.57	-0.26
11	3.31	3.17	+0.14
Average	2.62	2.70	-0.09

A paired difference was performed on the data set by NCASI. Once again, statistical evaluation indicated no difference between the two techniques. A relative accuracy (RA) calculation was performed according to the Federal Register. The relative accuracy was calculated to be 10.5 percent, well within the 20 percent limit specified in Performance Specification Test 5. In summary, no difference was found between Federal Reference Method 16 and Proposed Federal Reference Method 16A by the NCASI.

9.0 PERFORMANCE SPECIFICATION TEST

9.1 INTRODUCTION

EPA has established requirements under 40CFR60 and 40CFR51 for certain new and existing sources to install, operate and maintain continuous emission monitors. The initial intent of the regulations was to provide the operator the ability to monitor and "fine tune" his pollutant control device. Recently the regulations for some source categories have been modified to include use of continuous emission monitors for compliance with State and Federal Regulations. The Kraft pulp mill NSPS requires a continuous emission monitoring system to monitor TRS for operation and maintenance purposes. Compliance with the standard is determined by Reference Methods 16 and 16A.

As part of the NSPS regulations, continuous emission monitors had to pass a Performance Specification Test (PST) to insure they met certain design and specification requirements. These initial tests evaluated the performance characteristics of opacity, SO_2, NO_x, O_2 and TRS monitors. The evaluation of the monitoring system and compliance with the specification had the intended purpose of insuring reliable operation of a monitoring system once installed on the source. This was a one time certification procedure. The existing regulations do not provide specific procedures related to follow-up quality assurance evaluation.

On July 20, 1983, the U.S. Environmental Protection Agency (EPA) promulgated Performance Specification 5, "Specifications and Test Procedures for TRS Continuous Emission Monitoring Systems in Stationary Sources," in the Federal Register (48 FR 32986). The performance specification (PS) evaluates the acceptability of total reduced sulfur (TRS) continuous monitors as specified in the applicable regulations. The specification was proposed under the authority of Sections 111, 114, and 301 (a) of the Clean Air Act, as amended.

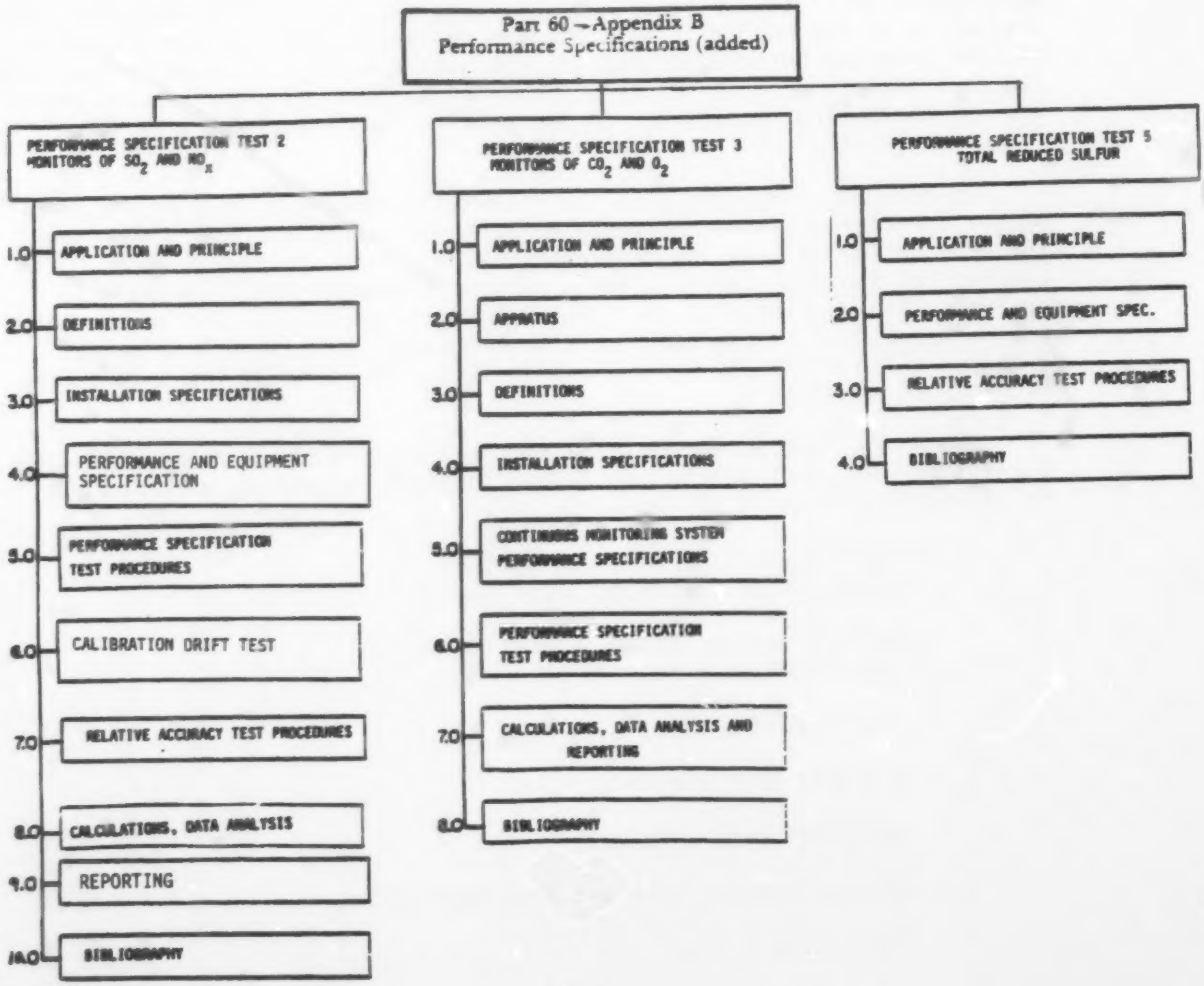
On May 25, 1983, EPA finalized rulemaking of Performance Specification 2 and 3 for SO_2, NO_x, CO_2 and O_2. The finalized rulemaking affected the following facilities:

- fossil-fuel-fired steam generators (construction commenced after Aug. 17, 1971);
- electric utility steam generating units (construction commenced after Sept. 13, 1978);
- nitric acid plants;
- sulfuric acid plants;
- petroleum refineries;
- primary copper, zinc and lead smelters;
- Kraft pulp mills;

and sources subject to Appendix P of 40 CFR Part 51. Consequently Kraft pulp mills are subject to both Performance Specification Tests 5 and 3 and parts of PS 2. The objective of this chapter is to discuss each of these specifications as applied to Kraft pulp mills.

The details contained within Performance Specification 5 apply to continuous monitoring systems measuring TRS. Similarly, the details contained within Performance Specification 3 are specific for O_2 or CO_2 continuous monitoring systems and those for SO_2/NO_x monitors are found in PS 2. Basically, each of these Performance Specifications consists of a set of operating criteria that each system installation must be shown to either meet or exceed. Table 5.1 outlines the sections for Performance Specification Tests 2, 3 and 5.

TABLE 9.1
PERFORMANCE SPECIFICATIONS FOR
SO_2/NO_x, O_2/CO_2 and TRS
CONTINUOUS EMISSION MONITORING SYSTEMS


Part 60 → Appendix B
Performance Specifications (added)
PERFORMANCE SPECIFICATION TEST 2 MONITORS OF SO_2 AND NO_x
1.0 APPLICATION AND PRINCIPLE
2.0 DEFINITIONS
3.0 INSTALLATION SPECIFICATIONS
4.0 PERFORMANCE AND EQUIPMENT SPECIFICATION
5.0 PERFORMANCE SPECIFICATION TEST PROCEDURES
6.0 CALIBRATION DRIFT TEST
7.0 RELATIVE ACCURACY TEST PROCEDURES
8.0 CALCULATIONS, DATA ANALYSIS
9.0 REPORTING
10.0 BIBLIOGRAPHY
PERFORMANCE SPECIFICATION TEST 3 MONITORS OF CO_2 AND O_2
1.0 APPLICATION AND PRINCIPLE
2.0 APPRATUS
3.0 DEFINITIONS
4.0 INSTALLATION SPECIFICATIONS
5.0 CONTINUOUS MONITORING SYSTEM PERFORMANCE SPECIFICATIONS
6.0 PERFORMANCE SPECIFICATION TEST PROCEDURES
7.0 CALCULATIONS, DATA ANALYSIS AND REPORTING
8.0 BIBLIOGRAPHY
PERFORMANCE SPECIFICATION TEST 5 TOTAL REDUCED SULFUR
1.0 APPLICATION AND PRINCIPLE
2.0 PERFORMANCE AND EQUIPMENT SPEC.
3.0 RELATIVE ACCURACY TEST PROCEDURES
4.0 BIBLIOGRAPHY

By imposing these requirements on each affected monitoring system, EPA has, in a sense, established a one time quality control check on the installed continuous emission monitor. After both field and laboratory evaluation programs with various brands and types of gaseous monitoring systems, EPA developed a list of operating parameters that were judged to be important factors in the successful operation of any system, regardless of the brand name of the unit and indifferent to the particular method of analysis. In addition to identifying important operating characteristics, EPA also identified the extent of deviation or tolerance allowable in each operational parameter. From this experience, EPA has developed a series of specifications by which the installed CEM must meet in order to be certified at that point in time. Table 9.2 lists those specifications for each parameter and affected facility as applied to Kraft pulp mills.

TABLE 9.2
PERFORMANCE SPECIFICATION REQUIREMENTS
KRAFT PULP MILLS

Parameter	Specification	
	Performance Specification 5 (TRS)	Performance Specification 3 (O_2/CO_2)
Accuracy	$\leq$ 20% of Mean Valve of Reference Method or 10% of the applicable std., whichever is greater	-
Calibration Drift (24 hour)		
Recovery Furnace (straight)	$\leq$ 5% (1.5ppm) at each of two points of the established span valve of 30 ppm for 6 out of 7 days.	$\leq$ 0.5% oxygen for 7 consecutive days.
Recovery Furnace (cross)	$\leq$ 5% (2.5ppm) at each of two points of the established span valve of 30 ppm for 6 out of 7 days.	$\leq$ 0.5% oxygen for 7 consecutive days.
Lime Kiln, Digestor, Brown Stack Washer, Evaporator, Oxidation or Stripper Systems	$\leq$ 5% (1.5ppm) at each of two points of the established span valve of 30 ppm for 6 out of 7 days.	$\leq$ 0.5% oxygen for 7 consecutive days.
Cycle of Operation	Each 15 minute period (sampling, analysis and data recording)	Each 15 minute (Sampling, analysis, and recording)

Unlike other specifications, Performance Specification Test 5 references several sections of Performance Specification Test 2 - Specification and Test Procedures for SO_2 and NO_x Continuous Emission Monitoring Systems in Stationary Sources. PS 2 discusses the mechanics of performing a PST. PS 5 references these procedures found in PS2. The following section discusses in detail the implications and influence of PS 2 on PS 5.

9.2 PERFORMANCE SPECIFICATION TEST 5

9.2.1 Reference to PS 2

> 1. *Applicability and Principle.*
>
> 1.1 Applicability. This specification is to be used for evaluating the acceptability of total reduced sulfur (TRS) and whenever specified in an applicable subpart of the regulations. (At present, these performance specifications do not apply to petroleum refineries, Subpart J).) Sources affected by the promulgation of the specification shall be allowed 1 year beyond the promulgation date to install, operate, and test the CEMS. The CEMS's may include O_2 monitors which are subject to Performance Specification 3 (PS 3).
>
> The definitions, installation specifications, test procedures, and data reduction procedures for determining calibration drifts (CD's) and relative accuracy (RA), and reporting of PS 2, Sections 2, 3, 4, 5, 6, 8, and 9 also apply to this specification and must be consulted. The performance and equipment specifications do not differ from PS 2 except as listed below and are included in this specification.
>
> 1.2 Principle. The CD and RA tests are conducted to determine conformance of the CEMS with the specification.

Section 1.0 defines applicability and principle as it relates to Performance Specification 5. Those sources subject to PS5 are outlined in the Subparts (except Subpart I) requiring monitoring of total reduced sulfur (TRS). If applicable, the source has one year from data of promulgation, July 20, 1983, to install, operate and test the CEMs. The test evaluation consists of a calibration drifts (CD's) and relative accuracy (RA) determination.

Two important principles are discussed in Sections 1.1 and 1.2 of PS5 which have a great impact on the performance and evaluation of installed TRS CEMs:

- Reference to Sections 2.0, 3.0, 4.0, 5.0, 6.0, 8.0 and 9.0 of Performance Specification 2 - Specification and Test Procedures for SO_2 and NO_x Continuous Emission Monitoring Systems in Stationary Sources.

- Conformance Specification (CD & RA) for TRS CEMs.

Within PS2, guidelines are given addressing definitions (2.0) installation and measurement location (3.0), performance and equipment specification (4.0), PST procedures (5.0), CEMs calibration drift prodedure (6.0), equations (8.0) and reporting (9.0). PS2 is applicable to SO_2 and NO_x CEMs and their certification. Within PS5, Sections 1.0 references those sections of PS2 and therefore are applicable to TRS CEMs certification.

9.2.2 Definition of TRS CEM System

Within Section 2.0 of PS2 we find guidance on the definitions of continuous emission monitoring system (CEMs) and span value. Under Section 2.1 of PS2, a CEMs is defined as:

> 2.1 Continuous Emission Monitoring System: "The total equipment required for the determination of a gas concentration or emission rate."

This definition incorporates the diluent monitor as part of the continuous emission monitoring system. As defines in Section 1.2 of PS5, the calibration drift (CD) and the relative accuracy (RA) test are conducted to determine conformance of the CEMs with the specification. Consequently, the RA test is performed on the CEMs, which includes the diluent monitor. Therefore, no individual RA test is required on the diluent monitor.

9.2.3 Span Value Definition

Secondly, guidance is given under Section 2.0 of PS5 dealing with the definition of span value. Under Section 2.4 of PS2, it defines span value as:

> 2.4 Span value: "The upper limit of a gas concentration measurement range specified for affected source categories in the applicable subpart of the regulations."

In this context, span value is the full range of the TRS monitoring system. For Kraft pulp mills, the span values for the TRS monitors are listed in Table 9.3.

TABLE 9.3
SPAN VALUES
KRAFT PULP MILLS TRS/O_2 MONITORS

Affected Facility	Pollutant	Span Valve
Recovery Furnace		
Straight Recovery	TRS	30ppm
	O_2	20%
Cross Recovery	TRS	50ppm
	O_2	20%

The span value of a TRS CEM should not be confused with the "span value" of a gas cylinder used to evaluate an installed CEM or the internal "span value" of a standard used to evaluate the performance of a CEM.

9.2.4 TRS CEM Installation and Measurement Location

> 3.1 The CEMS Installation and Measurement Location. Install the CEMS at an accessible location where the pollutant concentration or emission rate measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility or at the measurement location cross section. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see Section 7). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established. the Administrator may require the CEMS to be relocated.
>
> Suggested measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

Guidance is given within Section 3.1 of PS2 in reference to CEM installation and measurement location. In essence, it is the responsibility of the source to verify that the TRS CEM is located at a point that is representative or can be corrected so as to be representative of total emissions from the affected facility. The source must determine if stratification exists at the sampling location and if the sample extracted would be a "representative" sample.

9.2.4.1 Stratification Determination -

This is usually addressed in the permit and determined by velocity traverse or utilization of portable TRS monitors. Gaseous samples must be obtained from a sampling location that provides measurement which are representative of the total effluent. The key word in determining to what extent a sample may be considered representative is stratification. Stratification is defined within the Code of Federal Regulations as a condition (for any point more than 1.0 meter from a stack wall) whereby a concentration at any point differs from the average concentration in the stack by more than 10%. Algebraically, the existence of stratification is verified if the following relationship is found to occur:

$$\frac{|C_{ip} - \bar{C}_i|}{C_i} > 0.10$$

where c_i = average concentration of component i over the stack cross-section

C_{ip} = concentration of component i at the particular point p (greater than 1.0 meter from the wall) within the same stack cross-section

If no stratification exists at a given cross-section, then the sample is considered to be directly representative of the complete cross-sectional area of that stack and, therefore, directly representative of the total emissions. However, if stratification does exist, the sample from a given point may not be representative of the complete cross-sectional area, but that measurement can still be corrected to be representative of the total emissions.

The best assurance of non-stratified sampling location is obtained by performing a sampling traverse of the stack cross-section in question. The existence of stratification is confirmed if the condition described by the above equation is observed at any point farther than 1.0 meter from the stack wall.

9.2.4.2 Traverse Points Location -

Section 3.2 of PS2, Reference Method (RM) measurement location and traverse points, address the location of the RM Measurement point and traverse points during Relative Accuracy (RA) testing.

> 3.2 Reference Method (RM) Measurement Location and Traverse Points. Select, as appropriate, an accessible RM measurement point at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least a half equivalent diameter upstream from the effluent exhaust or control device. When pollutant concentration changes are due solely to diluent leakage (e.g., air heater leakages) and pollutants and diluents are simultaneously measured at the same location, a half diameter may be used in lieu of two equivalent diameters. The CEMS and RM locations need not be the same.
>
> Then select traverse points that assure acquisition of representative samples over the stack or duct cross section. The minimum requirements are as follows: Establish a "measurement line" that passes through the centroidal area and in the direction of any expected stratification. If this line interferes with the CEMS measurements, displace the line up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 16.7, 50.0, and 83.3 percent of the measurement line. If the measurement line is longer than 2.4 meters and pollutant stratification is not expected, the tester may choose to locate the three traverse points on the line at 0.4, 1.2, and 2.0 meters from the stack or duct wall. This option must not be used after wet scrubbers or at points where two streams with different pollutant concentrations are combined.

This section of PS2 is also referenced in PS5. IN essence, it states that during the RA testing, the RM sample is extracted from the source by traversing the "measurement line" at three traverse points. If the "measurement line" is 2.4 meters and pollutant stratification is not expected, the tester may choose to locate the points on the line at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the "measurement line" is longer than 2.4 meters, then the tester can locate the points on the line at 16.7, 50.0 and 83.3 percent of the measurement line. This stipulation, as recorded in PS2 and referenced in PS5, require the RM (16 or 16A) to perform a sample traverse during RA determination.

9.2.5 Performance and Equipment Specification

Section 2.0, Performance and Equipment Specification, address the performance specifications for calibration drift (CD) and relative accuracy (RA). In particular, the calibration drift is determined separately for the pollutant and diluent monitor. The drift test and relative accuracy procedures provide a means of confirming the integrity of the monitoring system on the source.

9.2.5.1 Calibration Drift -

The drift test involves introducing zero and span gas into the monitoring system. This procedure is repeated over an 8 day period. The monitor response is compared to the known concentrations (zero, span) to determine calibration drift.

According to Performance Specification 5, manual adjustments to the monitor are allowed after each determination, unless the monitor manufacturer specifies a shorter interval for adjustments. Specifically, the 24 hour drift test involves an established sequence of steps, as illustrated in Table 9.4.

TABLE 9.4
ITINERARY INVOLVING CALIBRATION DRIFT DETERMINATION

Day	Procedure
1	- Introduction of zero gas; adjustment of monitor to produce a correct zero reading. - Introduction of span gas; adjustment of monitor to produce a correct span value.
2	- Introduction of zero gas; record monitor response; adjust to zero, if needed. - Introduction of span gas; record monitor response; adjust to correct span value, if needed.
3-7	- Repeat sequence of steps performed during day 2.
8	- Introduction of zero gas; record monitor response; adjust to zero, if needed. - Introduction of span gas; record monitor response; end of calibration drift test.

Table 9.5 illustrates the Field Data Sheet for Calibration Drift Determination.

TABLE 9.5
CALIBRATION DRIFT DETERMINATION
ZERO/SPAN

Day	Date and Time	Calibration Value	Monitor Value	Difference	Percent of Span Value
1					
2					
3					
4					
5					
6					
7					
8					
1					
2					
3					
4					
5					
6					
7					
8					

$$\text{Calibration Drift (\%)} = \left[\frac{(\pm\text{Difference, ppm})}{(\text{Monitor Span value, ppm})}\right] \text{X } 100$$

During the Calibration Drift Test, the recorder should be offset (10%) to allow for negative drift. The 24 hour drift test requires 8 sets of zero and span measurements to facilitate 7 zero and calibration drift determinations. The procedure prescribed by Performance Specification 2 requires adjustments to the zero and span values following the respective zero and span measurements. Provided that this procedure is followed, the individual zero drift values are calculated as the zero value measured at the end of the 24 hour interval, minus the correct zero value. In the same manner, the calibration drift is the span value at the end of the 24 hour interval minus the correct span value. The adjustment of the zero value after the zero reading and before the span reading automatically removes the effects of zero drift on the span measurements. Thus, no further correction of the span measurements is necessary.

The Calibration Drift requirements are written in terms of per cent of monitor span value for each individual day. Mathematically, this is expressed by the following equation:

$$\text{Calibration Drift (\%)} = \left[\frac{(\pm\text{Difference, ppm})}{(\text{Monitor span value,ppm})}\right] \text{X100}$$

9.2.5.2 Accuracy (Relative) -

In the majority of cases, the term accuracy refers to the extent with which a measured value agrees with the actual or correct value. However, for continuous monitoring systems measuring TRS, the accuracy is determined as the degree with which the continuous monitor's measurement of the pollutant (O_2 corrected) agrees with the coincident measurement of the pollutant by an EPA Reference Method (O_2 corrected). Therefore, the accuracy of the continuous monitor is not necessarily measured in terms of an actual or known value but rather in terms of a second, independent measurement. For that reason the accuracy specification is termed "relative accuracy", i.e. relative to the value obtained by a Reference Method determination. As indicated earlier, relative accuracy is calculated using three variables:

- algebraic mean difference between monitor and reference method concentration measurements;
- 95% confidence interval (precision estimate associated with the determination of the mean difference); and
- mean concentration of the reference method.

Mathematically, this can be expressed by the following equation:

$$\% \text{ Relative Accuracy} = \frac{|x| + C.I._{95\%}}{[RM_{avg}]} \quad X100$$

where:

$|x|$ = absolute mean difference, for a series of tests, between monitor value and reference method value, corrected for oxygen;

$C.I._{95\%}$ = 2.5 percent error confidence coefficient;

$[RM_{avg}]$ = Average Reference Method value, oxygen corrected, for a series of tests.

The Reference Method TRS value and the CEM TRS value are both corrected for oxygen, according to the following equation:

$$C_{corr} = C_{meas} \left[\frac{(21-X)}{(21-Y)}\right]$$

whereas:

C_{corr} = the concentration corrected for oxygen.
C_{meas} = the concentration uncorrected for oxygen.
X = the volumetric oxygen concentration in percentage to be corrected to (8 percent for recovery furnaces and 10 percent for lime kilns, incinerators or other devices).
Y = the measured 12 hour average volumetric oxygen concentration.

The performance specifications for TRS CEMs are addressed in terms of calibration drifts and relative accuracy for TRS and calibration drifts for diluent monitors. In recent years, many of the performance specification requirements for gaseous CEMs have been eliminated. Table 9.6 illustrates the history of the performance specification requirement for each of the pollutants.

It is interpreted by the present regulations that many of the previous requirements were more long term quality assurance oriented, therefore would be addressed during later promulgated quality assurance regulations.

TABLE 9.6
PERFORMANCE SPECIFICATION REQUIREMENTS
REGULATORY CHANGES

	Performance Specification 2 (SO_2/NO_x)		Performance Specification 3 (O_2/CO_2)		Performance Specification 5 (TRS)
Parameter	1975[1]	1983[2]	1975[1]	1983[2]	1983[3]
Accuracy	X	X	-	X	X
Calibration Error	X	-	-	-	-
Zero Drift (2 hours)	X	-	X	-	-
Zero Drift (24 hours)	X	X	X	X	X
Calibration Drift (2 hours)	X	-	X	-	-
Calibration Drift (24 hours)	X	X	X	X	X
Response Time	X	X	X	X	-
Operational Period	X	X	X	X	-

1. Federal Register: 10/06/75 40 FR 46240
2. Federal Register: 5/25/83 48 FR 23608
3. Federal Register: 7/20/83 48 FR 32986

The mechanics of performing a relative accuracy determination involves a series of planned steps, as outlined in Table 9.7.

TABLE 9.7

PERFORMANCE SPECIFICATION TEST 5 FUNCTIONS

Time	Activity
6:00 A.M	I. Stratification Determination
7:00 A.M.	II. Assemble Sampling Train o Particle Removal System o SO_2 removal system o Permeation tubes in calibrator 24 hrs prior to test? o Chromatogram showing calibration gases with and without CO_2. o Chromatogram showing separation of SO_2 from reduced sulfur components? o All measurement/flow gauge calibrated and certificates sheets available.
8:00 A.M.	III Pre-Test Functions o Leak test sampling train o Upstream of pump o Downstream of pump o Calibration curve generated at 3 levels for H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$ o Calibration of dilution system to develop dilution factor using H_2S.
9:00 A.M.	IV Test Functions o Insert probe into stack o Pull sample through conditioning system for approx. 15 mins. o Commence traversing and sampling o Sample run involves 16 individual analyses over a period of not less than 3 hrs. or more than 6 hrs. o Orsat collected

TABLE 9.7 (Continued)

PERFORMANCE SPECIFICATION TEST 5 FUNCTIONS

Time	Activity
12:00 noon	V. Post-Test Functions
	o Leak check of total system
	o Sample line loss determination using H_2S at the level of the applicable standard
	o Correction factor developed
	o Recalibration after each run, or each series of runs made within 24-hours
	o Preliminary concentration determination
1:00	VI. Repeat for other test runs
7:00 P.M.	VII. Calculations

Once the Relative Accuracy test is complete, a Field Relative Accuracy Data sheet should be completed as part of the test report. Following is an example of a typical Field Relative Accuracy Data Sheet.

FIELD RELATIVE ACCURACY
DATA SHEET

Company ________________________ Date ____________________

Address ________________________ Analyst __________________

Company Contact _________________ Sample Location ____________

I. Field Data

Run #	Time	Total Reduced Sulfur (TRS) (ppm)		
		CEM Concentration (O_2 Corrected)	Reference Method (O_2 Corrected)	Difference
1				
2				
3				
4				
5				
6				
7				
8				
9				
Avg.				

II. Calculation

$$\% \text{ Relative Accuracy} = \frac{|\bar{X}| + C.I_{95\%}}{[RM_{avg}]} \times 100$$

$$= \frac{\_\_\_\_\_ + \_\_\_\_\_}{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} \times 100$$

$$= \frac{\_\_\_\_\_\_\_\_}{\_\_\_\_\_\_\_\_\_\_\_\_}$$

Test 1 __________
Test 2 __________
Test 3 __________

III. Acceptance

% Relative Accuracy $\leq$ 20% of mean value of Reference Method?

_____ Yes
_____ No

% Relative Accuracy 10% of the applicable standard?

_____ Yes
_____ No

IV. Recovery Data

% Recovery $\leq$ 20% ?

_____ Yes
_____ No

FIELD RELATIVE ACCURACY
DATA SHEET

Company ____________________ Date ____________________

Address ____________________ Analyst ____________________

Company Contact ____________________ Sample Location ____________________

I. Field Data

Run #	Time	Total Reduced Sulfur (TRS) (ppm)		
		CEM Concentration (O_2 Corrected)	Reference Method (O_2 Corrected)	Difference
1				
2				
3				
4				
5				
6				
7				
8				
9				
Avg.				

II. Calculation

$$\% \text{ Relative Accuracy} = \frac{|X| + C.I_{95\%}}{[RM_{avg}]} \times 100$$

$$= \frac{\_\_\_\_ + \_\_\_\_}{\_\_\_\_\_\_\_\_\_\_} \times 100$$

$$= \frac{\_\_\_\_\_\_\_\_}{\_\_\_\_\_\_\_\_\_\_}$$

Test 1 __________
Test 2 __________
Test 3 __________

III. Acceptance

% Relative Accuracy $\leq$ 20% of mean value of Reference Method?

______ Yes
______ No

% Relative Accuracy 10% of the applicable standard?

______ Yes
______ No

IV. Recovery Data

% Recovery $\leq$ 20% ?

______ Yes
______ No

9.3 PERFORMANCE SPECIFICATION 3 - SPECIFICATION AND TEST PROCEDURES FOR O_2 AND CO_2 CONTINUOUS EMISSION MONITORING SYSTEMS

9.3.1 Introduction

Performance Specification Test 3 - Performance Specifications and Specification Test Procedures for Monitors of CO_2 and O_2 from Stationary Sources, was originally promulgated October 6, 1975 in the Federal Register as part of Appendix B of 40 CFR 60. Concurrent with their promulgation, Performance Specification Test 1 for opacity continuous emission monitors and Performance Specification Test 2 for SO_2 and NO_x continuous emission monitors were also mandated.

The basic intent of the performance specifications was to evaluate the continuous emission monitoring system on the source under field conditions to determine its conformance with applicable specifications.

Because the Standard of Performance for Kraft pulp mills, relating to total reduced sulfur emissions, are 12-hour average TRS concentrations corrected to a percent oxygen, oxygen must also be monitored on a continuous basis. The equation reflecting this requirement is:

$$C_{corr} = C_{meas} \left[\frac{21 - X}{21 - Y} \right]$$

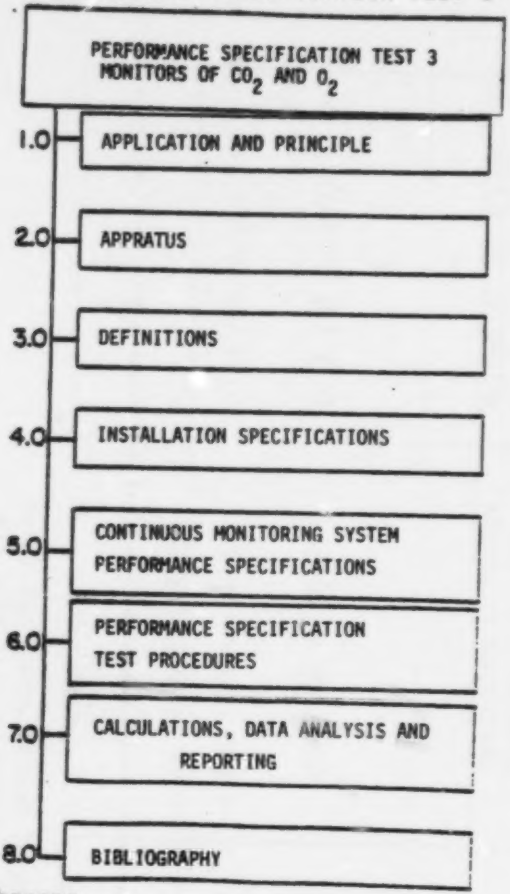
Where:

C_{corr} = the concentration corrected for oxygen;
C_{meas} = the concentration uncorrected for oxygen;
X = the volumetric oxygen concentration in percentage to be corrected to (8 percent for recovery furnaces and 10 percent for lime kilns, incinerators, or other devices); and
Y = the measured 12-hour average volumetric oxygen concentration.

As required by the regulations, O_2 continuous emission monitors must pass Performance Specifications Test 3.

Basically, the performance specifications consists of a set of operating criteria that each system installation must be shown to either meet or exceed. These specifications were judged to be important factors in the successful operation of any particular system. Table 9.8 illustrates the divisions of Performance Specification Test 3.

TABLE 9.8
PERFORMANCE SPECIFICATION TEST 3


PERFORMANCE SPECIFICATION TEST 3
MONITORS OF CO_2 AND O_2
1.0
APPLICATION AND PRINCIPLE
2.0
APPRATUS
3.0
DEFINITIONS
4.0
INSTALLATION SPECIFICATIONS
5.0
CONTINUOUS MONITORING SYSTEM PERFORMANCE SPECIFICATIONS
6.0
PERFORMANCE SPECIFICATION TEST PROCEDURES
7.0
CALCULATIONS, DATA ANALYSIS AND REPORTING
8.0
BIBLIOGRAPHY

9.3.2 Regulatory Changes

The performance specification requirements, when originally promulgated, addressed drift test (2 and 24 hour) for both zero and span, response time and operational test period. As with PS_2, PS_3 did not specify design criteria for CO_2 and O_2 analyzers.

On January 26, 1981, revisions to PS3 were proposed in the Federal Register. The difference between the 1975 promulgated specifications and the 1981 was the addition of a relative accuracy test. U.S. EPA felt that if the CO_2 or O_2 analyzer was not part of the continuous emission monitoring system, as covered under PS2, then a relative accuracy determination was needed.

The promulgated specifications were published in the Federal Register on May 25, 1983. The relatives accuracy requirements were retained for those CO_2 or O_2 analyzers not covered under PS2. However, the 2-hour drift test along with the response time and operational test period were not referenced in the May 25, 1983 regulations. Table 9.9 illustrates the regulatory changes made between 1975 and 1983.

TABLE 9.9
PERFORMANCE SPECIFICATION TEST 3
REGULATORY CHANGES

Parameter	10/6/75 (40 FR 46268) Promulgated	1/26/81 (46 FR 8364) Proposed Revision	5/25/83 (48 FR 23610) Promulgated Revisions
Relative Accuracy	—	20% of mean valve of reference method test data, or 1.0 present O_2 or CO_2, whichever is greater.	20% of mean valve of reference method test data, or 1.0 present O_2 or CO_2, whichever is greater.
Calibration Error	—	—	—
Drift Test			
Zero			
- 2-hour	0.4% (O_2 or CO_2)	-	-
- 24-hour	0.5% (O_2 or CO_2)	0.5% (O_2 or CO_2)	0.5% (O_2 or CO_2)
Span			
- 2-hour	0.4% (O_2 or CO_2)	-	-
- 24-hour	0.5% (O_2 or CO_2)	0.5 (O_2 or CO_2)	0.5% (O_2 or CO_2)
Response Time	10 minutes (max.)	10 minutes (max.)	—
Operational Period	168 hours	168 hours	—

*Each parameter determined from a series of tests; numerical value is the sum of the absolute value of the arithmetic mean plus the 95% confidence interval for the associated tests.

9.3.3 Interpretation of Performance Specification Test 3

9.3.3.1 Principle and Application -

Performance Specification Test 3 is used for evaluation of acceptability of O_2 and CO_2 continuous emission monitors (CEM's) at the time of or soon after installation and whenever specified in an applicable subparts of the regulations. The specifications apply to O_2 or CO_2, monitors that are not included under Performance Specification 5 (PS5).

The authors of PS3 intended the regulations to apply only to those monitors not used to report emissions in units of the standard. For example, Kraft pulp mills report emissions in ppm of TRS, corrected to a percent oxygen. In this configuration, the output of the TRS continuous emission monitoring system corrects to a percent oxygen. The oxygen monitor is therefore a part of the total TRS CEM system. As such, relative accuracy of the TRS monitoring system incorporates error associated with the O_2 analyzer.

9.3.3.2 Apparatus

This section of PS3 addresses the calibration gas mixtures to be used in evaluative calibration drift determination. In particular, the gas cylinder concentrations should be known concentrations of carbon dioxide or oxygen in nitrogen or air. The calibration gas mixture shall be at two levels as indicated in Table 9.10.

TABLE 9.10
CALIBRATION GAS MIXTURE LEVELS

Range	O_2/CO_2
Low Level	0-20% of Span Valve
High Level	50-100% of Span Valve

Triplicate analysis of the gas mixture should be performed within two weeks prior to use using Federal Reference Method 3.

9.3.3.3 Definitions

The total continuous emission monitoring system involves the total equipment required for determination of CO_2 or O_2. Since most TRS CEMs are extractive, the system would involve the side stream of gas taken from the main gas stream for O_2 analysis, the analyzer itself and the data recording system.

9.3.3.4 Installation Specification -

If the O_2 continuous emission monitoring system is not part of the TRS CEM, then it shall be installed at a sampling location where measurements that can be made are representative of the effluent gases sampled by the pollutant continuous monitoring system(s). Conformance with this requirement may be accomplished in any of the following ways:

(1) The sampling location for the diluent system shall be near the sampling location for the pollutant continuous monitoring system such that the same approximate point(s) (extractive systems) is sampled; and

(2) The diluent and pollutant continuous monitoring system may be installed at different locations if the effluent gases at both sampling locations are nonstratified and there is no in-leakage occuring between the sampling points.

For TRS monitoring systems, the O_2 is normally taken as a side stream of the main extractive sample. As such, both the TRS monitor and the O_2 monitor would see the same gas stream. Consequently, the sampling point location is not a critical factor.

9.3.3.5 Continuous Monitoring System Performance Specifications -

As specified in the regulations, the only specifications the O_2 monitor must meet are illustrated in Table 9.11.

TABLE 9.11
PERFORMANCE SPECIFICATION

Parameter	Specifications 5/25/83 48 FR 23600
Drift Test (24 hour)	
Zero	0.5%
Span	0.5%
Relative Accuracy*	20% of mean valve of reference method test data or 1.0 percent O_2, whichever is greater

* Only applies to those O_2 and CO_2 monitors not covered under Performance Specification 2 (PS2).

9.3.3.5.1 Accuracy (Relative) -

The Relative Accuracy (RA) test provides a means of confirming the integrity of the O_2 continuous emission monitoring system. As discussed earlier, relative accuracy requirements are not required for installed O_2 continuous emission monitors used in conjunction with pollutant monitors to generate a value in terms of units of the standard. For Kraft pulp mills, this involves correcting TRS emissions to a percent oxygen value. Thus, the oxygen monitor is part of the TOTAL CEM system. Any inaccuracies in the O_2 monitors will be incorporated in the total system Relative Accuracy Test for the pollutant monitor.

9.3.3.5.2 Calibration Drift Test -

However, there are calibration drift requirements which are determined separately for the pollutant and diluent monitor.

The drift test involves introducing zero and span gas into the monitoring system. This procedure is repeated over an 8 day period. The monitor response is compared to the known concentration (zero, span) to determine a calibration drift error. The calibration gas mixture concentrations should be those specified in Table 9.10.

According to the Performance Specification Test , manual adjustments to the monitor are allowed at 24-hour intervals, unless the monitor manufacturer specifies a shorter interval for adjustments. Table 9.12 summarizes the sequence of steps performed in a drift test determination.

TABLE 9.12
ITINERARY INVOLVING CALIBRATION DRIFT DETERMINATION

Day	Procedure
1	- Introduction of zero gas; adjustment of monitor to produce a correct zero reading. - Introduction of span gas; adjustment of monitor to produce a correct span value.
2	- Introduction of zero gas; record monitor response; adjust to zero, if needed. - Introduction of span gas; record monitor response; adjust to correct span valve, if needed.
3-7	- Repeat sequence of steps performed during day 2.
8	- Introduction of zero gas; record monitor response; adjust to zero, if needed. - Introduction of span gas; record monitor response; End of calibration drift test .

Table 9.13 illustrates the Field Data Sheet for Calibration Drift Determination.

TABLE 9.13
FIELD DATA SHEET
CALIBRATION DRIFT DETERMINATION

Day	Date and Time	Calibration Value	Monitor Value	Difference	Percent of Span Value
1					
2					
3					
4					
5					
6					
7					
8					
1					
2					
3					
4					
5					
6					
7					
8					

$$\text{Calibration Drift (\%)} = \frac{(\pm\text{Difference, ppm})}{(\text{Monitor Span value, ppm})} \quad \text{X } 100$$

During the calibration drift test determination, the recorder should be offset (-10%) to allow for negative drift. The 24-hour drift test requires 8 sets of zero and span measurements to facilitate 7 zero and calibration drift determinations. The procedure prescribed by Performance Specification 2 requires adjustments to the zero and span values following the respective zero and span measurements. Provided that this procedure is followed, the individual zero drift values are calculated as the zero value measured at the end of the 24 hour interval, minus the correct zero value. In the same manner, the calibration drift is the span value at the end of the 24 hour interval minus initial reading (before the span reading automatically removes the effects of zero drift on the span measurements).

9.3.3.6 Calculations, Data Analysis and Reporting -

The calibration drift requirements are written in terms of per cent of monitor span value for each individual day. Mathematically, this is expressed by the following equation:

$$\text{Calibration Drift (\%)} = \left[\frac{(\ \pm\text{Difference, ppm}\ )}{(\ \text{Monitor span valve,ppm}\ )}\right] \text{X } 100$$

10.0 EXCESS EMISSION REPORTS

10.1 INTRODUCTION

The Environmental Protection Agency (EPA) and many state air pollution control agencies are rapidly expanding their programs involving recordkeeping and reporting requirements in association with emission monitoring programs and performance testing. This is due, in part, to new regulations pertaining to new and existing sources as outlined in 40 CFR 60 and 40 CFR 51 respectively. These regulations require "installation of monitoring equipment and performance testing...." and "for periodic reports and recordkeeping of nature and magnitude of such emissions." Likewise, Sections 113 and 114 of the Clean Air Act (CAA) as amended in 1977, involve the use of recordkeeping and reporting requirements as a means of enforcement of emission standards.

Historically, the reporting requirements have involved "excess emissions" over and above emission standards as indicated by the continuous emission monitor. The initial intent of the regulations was to provide the source operators, through the use of continuous emission monitoring, the ability to monitor and "fine tune" his pollution control device. Only those emissions above a regulated standard were reported through the quarterly excess emission report (EER) to the control agency. The EER should contains information on number of excess emission over a standard, time and duration of those excess emissions, reason codes for excess emissions and corrective/preventive action taken to reduce those emissions. As personnel and money limits the feasibility of on-site inspections, the EER becomes an important "feedback" system for both the source and the regulatory agency. The EER becomes a tracking tool by which agency personnel can evaluate both the control equipment and CEM performance. The EER provides a useful function for both the sources being regulated and the regulatory agency. For the source, the benefits are:

- to help ensure upper management awareness and attention of excess emissions through the formal requirement for source submittal of a summary of excursions. This hopefully increases the likelihood of the source's timely attention to the reduction of excess emissions; and
- as a tool in preventive maintenance/risk management/cost control programs and to flag deterioration of control equipment performance. In cases such as fuel burning, CEM data can be used to optimize continually the combustion process and control system performance, thus saving money and preventing pollution at the same time.

For the regulatory agency, the benefits are:

- as a screening tool, to identify sources experiencing frequent or continual excursions. Such sources can be subjected to additional attention in the form of phone calls, inspections, etc.

- in addition to identifying problem sources, to help pinpoint specific source components for special attention during an inspection;
- to document the severity (e.g., duration, magnitude, and frequency) of a source's excess emissions.. For example, EER data can provide supporting evidence of the long-term nature of violations, negating source claims of isolated problems;
- to document that a compliance test was performed during "non-representative" operating conditions;
- as support for issuing a Notice of Violation (NOV);
- to establish a data base for the development of agency policies and strategies (e.e., acid rain strategies);
- as the basis for assessing "good air pollution control practices;"
- as an alternative to agency inspections of sources as delineated in the Levels of Inspection; and
- to monitor the emissions and performance of a source subject to specific permit, consent decree, or administrative order requirements.

Data from the excess emission report can be entered into the CEM subset of the Compliance Data System (CDS). The CDS system forms the basis by which EPA tracks the compliance status of regulated sources. In order to make proper planning and budgetary decisions, periodic update of the CDS system is mandatory. The EER becomes the vehicle (outside of on-site inspections) by which the Agency can update the CDS system and monitor performance of both the pollution control equipment and the source's CEM system.

10.2 STANDARDIZED EXCESS EMISSION REPORT

In recent years, the standardized EER has not only been used to report excess emissions, but also provide other information associated with both control equipment and monitor performance. Such information as:

- excess drift determination;
- quarterly audit results;
- relative accuracy test;
- pollution control device operating parameters (pressure drop, milliamps, flow rates, etc.);
- "out-of-control" situations; and
- control equipment "baseline" information

has become routine report items on the EER. With limited resources and manpower, the EER becomes the "tracking" mechanism of monitor and control equipment performance during periods when the control Agency personnel are unable to perform on-site evaluations.

The EER has become a major part of the enforcement program of regulatory agencies. This new importance has shifted the initial intent of the EER as an indicator of emissions over a standard to a "continuous compliance" standard indicator. Consequently, present day interpretation of the regulations moves the EER from a historical document to a present day document. The present day EER form must provide needed information concerning "maintenance of compliance" as referenced in the regulations.

For stationary sources subject to NSPS continuous monitoring requirements, 40 CFR 60.7 requires submittal of a written report of excess emission for every calendar quarter.

Historically, the reporting requirements for NSPS sources (40 CFR Part 60) have involved a written report for any calendar quarter in which source emissions exceed the value of the standard. The emission value, as recorded by the CEM system (i.e., % opacity, ppm, lb/ton, etc.) must be recorded, as well as the duration (i.e., six minutes, 3 hours, 12 hours, etc.) of the excess emission. An excess emission is defined as exceedance of the emission limit values over the time period specified by the subject standard.

Similarly, 40 CFR Part 51 requires some existing stationary sources to implement a continuous monitoring program and to provide quarterly excess emission reports (EERs). The minimum information required in the excess emission report is:

1. The magnitude, duration and date of excess emissions;
2. The identification of each excess attributable to startups, shutdowns, and malfunctions;
3. The cause of any malfunction and the corrective action or preventive measures adopted;
4. The date, time, and duration of any monitor outage for reasons other than zero and span checks;
5. The reason for monitor outage and corrective action taken;
6. If there are no excess emissions and no monitor outages, this information must also be reported.

Those NSPS sources required to submit EERs are listed in Table 10.1.

TABLE 10.1
NSPS SOURCES REQUIRED TO SUBMIT EXCESS EMISSION REPORTS (EERs) TO REGULATORY AUTHORITIES

Subpart	Source Category	Pollutant
D	Steam Generators	
	Solid Fossil Fuel	Opacity, SO_2, NO_x
	Liquid Fossil Fuel	Opacity, SO_2, NO_x
	Gaseous Fossil Fuel	NO_x
Da	ELECTRIC UTILITY STEAM GENERATING UNITS	
	Solid Fossil Fuel	Opacity, SO_2 (at inlet and outlet of control device), NO_x
	Liquid Fossil Fuel	Opacity, SO_2 (at inlet and outlet of control device), NO_x
	Gaseous Fossil Fuel	NO_x
G	NITRIC ACID PLANTS	NO_x
H	SULFURIC ACID PLANTS	SO_2
J	PETROLEUM REFINERIES	
	FCCU	Opacity, CO
	Combustion of Fuel Gases	SO_2 or H_2S
	Sulfur Recovery Plant	SO_2, H_2S, TRS,
P	PRIMARY COPPER SMELTERS	Opacity, SO_2
Q	PRIMARY ZINC SMELTERS	Opacity, SO_2
R	PRIMARY LEAD SMELTERS	Opacity, SO_2
Z	FERROALLOY PRODUCTION FACILITIES	Opacity
AA	STEEL PLANTS: ELECTRIC ARC FURNACES	Opacity

TABLE 10.1 (Continued)
NSPS SOURCES REQUIRED TO SUBMIT
EXCESS EMISSION REPORTS (EERs) TO REGULATORY AUTHORITIES

Subpart	Source Category	Pollutant
BB	KRAFT PULP MILLS	
	Recovery Furnace	Opacity TRS (dry basis)
	Lime kiln, digester system, brown stock washer system, multiple effect evaporator system, black liquor oxidation system, or condensate stripper system.	TRS (dry basis)
HH	LIME MANUFACTURING PLANTS	
	Rotary Lime Kilns	Opacity

For Subpart BB, Standards of Performance for Kraft Pulp Mills, EER's must be submitted to the regulatory authority when emission levels are exceeded for affected facilities within the subpart. Table 10.2 lists those affected facilities in the Kraft pulp mill which require reporting exceedances.

Similarly, 40 CFR 51 requires that all existing stationary sources, directed to implement a continuous monitoring program, must also provide quarterly excess emission reports (EERs). This reporting requirement, as originally conceived in the September 11, 1974, specified not only quarterly reporting of excess emissions but also quarterly submittal of all monitoring results. This was later revised to require the reporting of only excess emissions.

As defined, excess emission of TRS for each affected facility in Subpart BB, Kraft Pulp Mills, are defined in terms of emissions over a standard for a twelve hour average period. The regulations do not, however, specify the definition of a 1-hour average to comprise the 12-hour average. As written, the average may be calculated either by:

(1) integrating over the hourly intervals; or

(2) arithmetic averaging over the hourly intervals.

TABLE 10.2
KRAFT PULP MILLS
EXCESS EMISSION REPORTING REQUIREMENTS

Source Category	Affected Facility	Pollutant	Emission Level	Monitoring Requirement	CEM Reporting Requirements
Subpart BB - Kraft Pulp Mills Proposed/effective 9/24/76 (41 FR 42012) Promulgated 2/23/78 (43 FR 7568) Revised 8/7/78 (43 FR 34784)	Recovery furnace	Particulate	0.044 gr/dscf (0.10 g/dscm) corrected to 8% oxygen	No requirement	
		Opacity	35%	Continuous	EER for six-minute averages in excess of 35% if period with violations are greater than 6% of six-minute periods
		TRS (a) straight recovery	5 ppm by volume corrected to 8% oxygen	Continuous	EER for twelve-hour averages in excess of 5 ppm time periods with violations are greater than of total twelve-hour periods
		(b) cross recovery	25 ppm by volume corrected to 8% oxygen		EER for twelve-hour averages in excess of 25 pp time periods with violations are greater than total twelve-hour periods
	Smelt dissolving tank	Particulate	0.2 lb/ton (0.1 g/kg)BLS	No requirement	Note: BLS = BLACK Liquor Solids
		TRS	0.0168 lb/ton (0.0084 g/kg)BLS	No requirement	
	Lime kiln	Particulate (a) gaseous fuel	0.067 gr/dscf (0.15 g/dscm) corrected to 10% oxygen	No requirement	
		(b) liquid fuel	0.13 gr/dscf (0.30 g/dscm) corrected to 10% oxygen	No requirement	
		TRS	8 ppm by volume corrected to 10% oxygen	Continuous	EER for twelve-hour averages in excess of 8 ppm
	Digester, brown stack washer, evaporator, oxidation, or stripper systems	TRS	5 ppm by volume corrected to 10 oxygen	Continuous	EER for twelve-hour averages in excess of 5 ppm
			*exceptions; see standards	Effluent gas incineration temperature; scrubber liquid supply pressure and gas stream pressure loss	Report for all periods greater than five minute combustion temperature less than 1200°F

Guidance is given in Subpart D, Standards of Performance for Fossil Fueled Fired Steam Generators (FFFSG), associated with the definition of a 1 hour average. The regulation uses a minimum of "four equally spaced data points" for determining an hourly average. However, no guidance is given by the regulations in association to what constitutes a valid hour of emission data.

Excess emission reporting requirements for Kraft pulp mills also allow an accepted excess emission over the standard before it must be reported. The exemption states:

§60.283(a)(1)(ii):

> *"(e) The Administrator will not consider periods of excess emissions reported under paragraph (d) of this section to be indicative of a violation of § 60.11(d) provided that:*
>
> *(1) The percent of the total number of possible contiguous periods of excess emissions in a quarter (excluding periods of startup, shutdown, or malfunction and periods when the facility is not operating) during which excess emissions occur does not exceed:*
>
> *(i) One percent for TRS emissions from recovery furnaces.*
>
> *(ii) Six percent for average opacities from recovery furnaces.*
>
> *(2) The Administrator determines that the affected facility, including air pollution control equipment, is maintained and operated in a manner which is consistent with good air pollution control practice for minimizing emissions during periods of excess emissions."*

The EER is used by some regulatory agencies for enforcement actions; therefore, the report must be thorough and complete. A recent survey of 22 NSPS sources required to submit EER's to EPA regional offices revealed that only 25 percent of the required information was reported to the Federal or State authorities. All surveyed had omitted one or more of the following areas of information from the EER:

1) reason for the excess emissions;

2) action taken to reduce excess emissions; and

3) any malfunctions associated with the CEM system.

Another survey showed that CEM programs with good recordkeeping and reporting requirements also had demonstrated reliable CEM operations. This information has prompted EPA to examine the use of "standardized" EER's to facilitate ease and completeness of reported data. A standardized report format for process/ control equipment and excess emission information would provide the following benefits:

1) increase industry understanding of the EER requirements;

2) provide a correlation between "excess emission" and control or process monitoring malfunctions;

3) eliminate the need and cost for individual users and CEM system manufacturers to design special data handling and reporting systems;

4) reduce industries' effort in completing EERs and agencies' workload to review the reported data; and

5) identify data reliability.

Following is an example of a "standardized" EER form for Subpart BB, Kraft pulp mills.

EXCESS EMISSION REPORT
KRAFT PULP MILLS
SUBPART BB

Continuous Emission Monitoring Data
Quarterly Report

Report Period Ending Mar 31 ☐ June 30 ☐ Sept 30 ☐ Dec 31 ☐

Year 19__

I. General Information

1. Source ____________________
2. Address ____________________
____
____
3. Phone Number ( ) ____________________
4. Affected Facility ____________________
5. Control Device ____________________
6. Fuel Type ____________________
7. Person Completing Report (Print) ____________________
(Signature) ____________________
(Date) ____________________

THIS IS TO CERTIFY THAT, TO THE BEST OF MY KNOWLEDGE, THE INFORMATION PROVIDED ON THESE FORMS IS CORRECT AND ACCURATE.

8. Person responsible for review and integrity of report (Print) ____________________
(Signature) ____________________
(Title) ____________________
(Date) ____________________

II. Continuous Monitor Data

	Opacity	Total Reduced Sulfur (TRS)	
1. Manufacturer	____________	________________	
2. Model No.	____________	________________	
3. Serial No.	____________	________________	
4. Basis for Gas Measurement (wet or dry)	____________	________________	
5. Averaging Time	____________	________________	
6. Corrected to % O_2	XXXXXXXXXXXXXXX	________________	
7. Zero/Calibration Values	____________	________________	
Zero	____________%	________________	ppm
Cal	____________%	________________	ppm
8. Date of Last Performance Specification Test Passed	____________	________________	
9. Performance Specification Test	____________	________________	
Date	____________	________________	
10. Emission Limit	____________	________________	
11. Total Operating Time of Source During Reporting Period (minutes)	____________	________________	

III. Continuous Emission Monitor Excess Emission Data

Pollutant: ☐ Opacity ☐ TRS (Corrected % O_2) Process: ____________

Excess Emission Period						
Date	Time (24 hr clock)		Duration (minutes)	Average Value of Emissions During Excess ☐ % ☐ ppm	Reason for Excess Emissions	Corrective Action Taken
Day/Month/Year	Begin	End				

☐ No Excess Emissions During Reporting Period

IV. Continuous Emission Monitor Performance Data

Pollutant: ☐ Opacity ☐ TRS Process ____________

Monitor Downtime Period**			Duration (minutes)	Reason for Outage	Corrective Action Taken	Total Operating Time of Source (minutes) on Date of Monitor Downtime	Monitor* Availability (%) for Date
Date	Time (24 hr clock)						
Day/Month/Year	Begin	End					

$$\text{* Monitor Availability} = \frac{\text{CEM downtime during source operating time (Min)}}{\text{Source operating time (Min)}} \times 100$$

**Include periods of monitor equipment malfunction, non-monitor CEM equipment malfunction, or unknown causes.

☐ No CEM Downtime During Reporting Period

10.3 EXCESS EMISSION AGENCY REVIEW PROCESS

Once the EER is submitted by the source to the regulatory authority, it should be reviewed and entered into the CDS. To assist in this effort, the Stationary Source Compliance Division recently published a document entitled: "Technical Guidance on the Review and Use of Excess Emission Reports." The main objective of this document was the implementation, at the state and regional levels, of a methodical procedure to review and follow up on EERs.

The EER review involves a three-phase process:

- Phase 1 - Initial review and summary of EER data;
- Phase 2 - Confirmation of Phase 1 results, targeting of sources for follow up, and data input to the CEM subset of the Compliance Data System (CDS); and
- Phase 3 - Follow up comparison of CEM and other emission data, with potential recommendations for additional testing or compliance/enforcement actions.

An example of the proposed agency checklist for EERs can be found at the end of this section.

10.3.1 Phase 1 - Initial EER Review

During Phase 1, the agency reviewer evaluates the data for entry into the CDS. In particular, the reviewer addresses completeness and general acceptability of the EER for the following areas:

- Submittal of EER within 30 days after the end of each calendar quarter containing:
  (1) Excess emissions; and
  (2) Monitor system performance;
- Submittal of EER even if no excess emissions occurred within the quarter;
- Verification that the excess emission report includes:
  (1) The magnitude (averaged during the excess period, including any conversion factor(s) used), date, start and ending times, nature, cause and corrective action taken for each excess emission; specific identification of each period of excess that occurred during startups, shutdowns and malfunctions of the affected facility; the nature and cause (if known) of the malfunctions and corrective actions taken;

  (2) The date, start and ending times of each instance when the CEM was inoperative (except for zero and span checks, etc.), and description of the nature, cause and corrective action taken for each such period; and

  (3) Total operating time of source in the quarter.

10.3.2 Phase 2 - Targeting of Follow Up Action

Phase 2, verification of Phase 1 results, requires the control agency reviewer to identify if:

- completion of internal check and concurrent with phase 1;
- comparison of EER data with control agency targeting criteria; and
- entry of EER data into the CEM subset of the CDS.

Spot-checking of phase 1 data to concur with its results is normally a sufficient internal review. Once the internal check is completed, the percent availability for the industry operating time is compared to the agency action target level. If it does not fall within the preset target level, then follow-up action might be appropriate. The objective is to identify those sources which are indicating "non-compliance" more so than other reporting sources. These "targeted" sources would constitute some action on the part of the reviewing control agency. Once phase 2 review is completed, the control agency should notify the source of the results, whether positive or negative. This will help promote a cooperative effort between the source and the control agency.

Finally, during phase 2, the data is entered into the CEM subset of the CDS.

10.3.3 Phase 3 - Follow Up Activity

Phase 3 involves the follow up activities for those sources targeted in phase 2 of the review process. This may be done in the office or the field. In essence, the control agency personnel is determining the validity of the EER, through comparisons of other available data (inspection reports, stack test reports, etc.), to formulate a recommendation for an enforcement action.

Once the three phase review has been completed, the reviewer then signs the review checklist, indicating all necessary actions pertaining to this review process have beem completed.

Following is an example of an control agency reviewer checklist for Kraft pulp mill excess emission reports. The checklist is divided into three sections: (1) Abbreviated Reviewers Checklist; (2) Detailed Action Reviewers Checklist; and (3) Follow-up Action From Detailed Action.

EXCESS EMISSION REPORT
KRAFT PULP MILLS - SUBPART BB
ABBREVIATED REVIEWER'S CHECKLIST

Phase 1 Review ____________________ Name __________ Date

Phase 2 Review/
Subset Data Entry ____________________ Name __________ Date

Phase 3 Review/
CDS Action Entry ____________________ Name __________ Date

1.0. GENERAL INFORMATION

1.1 Company ____________________ ____________ Quarter ____________ Year

Plant/Unit ____________________ ____________________ Process

1.2 Timeliness (Must be postmarked within 30 days of quarter)

(a) Date Postmarked ____________________ (b) Days Late ____________________

2.0 COMPLETENESS (For EERs which cover multiple monitors, specify monitor when noting problem.)

	No Problem	Problem (Describe)
2.1 Excess Emissions (EEs) Information		
(a) Data Reported in Units of Applicable Standards (ppm, corrected to % O_2, or opacity)		
(b) Date and Time of Commencement of Excess Emission		
(c) Average Magnitude (ppm or opacity)		
(d) Identification of Excess Emissions Caused by Start-up, Shutdown, or Malfunction		
(e) Nature and Cause of Malfunction		
(f) Malfunction Corrective Action or Preventive Measures Taken		
(g) Affirmative Statement of NO Excess Emissions		
2.2 CEMS Performance Information		
(a) Date and Time Identifying Specific Periods During Which CEM was Inoperative		

	No Problem	Problem (Describe)
(b) Nature of Corrective Action/ System Repairs or Adjustments		
(c) Monitor % availability for date calculated		
(d) Affirmative Statement of NO Period of Downtime, Repair or Adjustment (include no CEMS modifications)		
2.3 Source Operating Time Noted		

3.0 EER DATA SUMMARY

3.1 Should This EER Be Reviewed For Possible Agency Follow-up?

Yes/No

Comments

3.2 Signature

(Print)

(Date)

EXCESS EMISSION REPORT
KRAFT PULP MILLS-SUBPART BB
DETAILED REVIEWERS CHECKLIST

Phase 1 Review ____________ ________
Name Date

Phase 2 Review ____________ ________
Name Date

Phase 3 Review ____________ ________
Name Date

1.0 GENERAL INFORMATION

1.1 Company ____________________ ________ ________
Quarter Year

1.2 Plant/Unit ____________________ ________________
Process

2.0 DATA SUMMARY FOR TRS/OPACITY EERs (USE SEPARATE FORM FOR EACH MONITOR)

2.1 CEMS Performance Per Quarter

Causes of CEMS Downtime	Total Downtime # of Incidents	 Total Mins.	Source Operating Time (Min)	% Availability*
Monitor Equipment Malfunction				
Non-monitor CEMS Equipment Malfunctions (i.e. Computer, Data Recorder etc.)				
Calibration/QA Audits				
Other				
Unknown Causes				
Average				

$$^*\%\text{ Availability} = \frac{\text{(CEM uptime during source operating time, min.)}}{\text{(source operating time, min.)}} \times 100$$

2.2 Emission Performance Per Quarter

Causes of Excess Emissions	Total Excess Emissions # of Incidents	 Total Mins.	Source Operating Time (Min.)	% Compliance*
Control Equipment Failures				
Process Problems				
Other				
Average				

$$^*\%\text{ Compliance} = \frac{\text{(Source Operating Time, min.) - (Excess Emissions, min.)}}{\text{(Source Operating Time, min.)}} \times 100$$

EXCESS EMISSION REPORT
KRAFT PULP MILLS-SUBPART BB
FOLLOW-UP REVIEWERS CHECKLIST

Phase 1 Review ____________ Name ________ Date

Phase 2 Review ____________ Name ________ Date

Phase 3 Review ____________ Name ________ Date

1.0 GENERAL INFORMATION

1.1 Company ______________________ ________ Quarter ________ Year

1.2 Plant/Unit ______________________ ________________

2.0 FOLLOW-UP ACTIVITY FROM DETAILED EER REVIEW

Follow-up Action	CEMS Problems		Emission Problems		Timeliness	Completeness
	TRS	OPACITY	TRS	OPACITY		
No Action						
Detailed EER Review Next Quarter						
Contact Source						
a. Telephone source						
b. Meet with source						
c. Req. addit. info.						
d. Req. addit. report						
e. Request corrective action						
f. Req. addit. test						
g. Request alt. monitoring						
h. Request specific O&M/QA procedures						
i. Other (Specify)						
Additional Surveillance						
a. VEO						
b. Inspection						
c. Audit						
d. Compliance Test						
e. Other						
Enforcement						
a. Warning Letter						
b. § 113 NOV						
c. § 113 Comp. Order						
d. Init. Civil Action						
f. Other (Specify)						

11.0 QUALITY ASSURANCE/QUALITY CONTROL

11.1 INTRODUCTION.

The primary objective of a Quality Assurance (QA) program for CEMs is to ensure that all data collected and reported are meaningful, precise and accurate within a stated acceptance criteria. The program should be strong, but flexible enough to allow continuing evaluation of its adequacy and effectiveness. This assessment provides an on-going corrective action system, as illustrated in Figure 11.1 of the QA program.

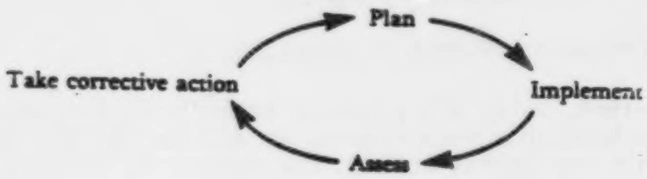


Figure 11.1 QA/QC Assessment

Consequently, the purpose of a quality assurance/quality control plan (QA/QC) is to describe the activities to be used in assessing the validity of installed CEM systems.

QA/QC activities involve both routine and periodic evaluation. Historically, these activities have been performed by the source as part of their own quality assurance program. Source QA/QC activities vary from source to source. Source QA/QC activities are not required by law. The only real QA activity required by law has been the Performance Specification Test (PST). It is within the PST that the monitoring system must pass minimum criteria standards in order for the system to be "certified". These initial tests evaluated the performance characteristics of the installed monitor to standard reference methods. It was the intended purpose of these procedures to ensure reliable operation of a monitoring system once it was installed on the source. The PST provided the regulatory agency information concerning the operation of the total CEM system as compared to the Reference Method. As such, the PST was a quality assessment check of the monitoring system. Likewise, the test provided the source operator/owner of the CEM system a means of evaluating the system to determine its applicability to that source environment. This, too, was a quality assessment check. What was lacking, however, was a continued check of the system after the PST. The PST is a one time certification procedure involving both the regulatory agency and the source.

As CEMs became an integral part of the enforcement activities of both EPA and State/local programs, it became imperative that some form of continued evaluation of the monitoring system occur to ensure its continued performance and reliabililty. This continued evaluation would assist the EPA and the State Agency in establishing CEM long term performance and reliability as part of their data base. Consequently, QA/QC activities involve both source and agency functions.

The main objective of this chapter is to present various elements as possible components of a QA/QC program associated with three organizations. They are:

- U. S. Environmental Protection Agency;
- Industry; and
- State Regulatory Agency.

11.2 U. S. EPA, PROPOSED APPENDIX F, PROCEDURE 1

On March 14, 1984, U. S. EPA proposed Appendix F, Procedure 1, addressing source quality assurance requirements as applied to "all CEMS installed under a subpart that designates CEMs as the Method for showing compliance with emission limits on a continuous basis. The regulation would apply to subpart Da, 40 CFR Part 60 (electric utility steam generating units for which construction is commenced after September 18, 1978). It would also apply to other subparts which may be proposed before or after proposal of Procedure 1, if the subpart requires the use of gas CEMS as the performance test method on a continuous basis." The intent of the proposed rule is to require source owners of gas CEMs to self-evaluate periodically the monitor's precision and accuracy. The proposed rule requires the source owner or operator to:

- Develop and implement a quality control program that includes written procedures for key CEMs operations;
- Calculate monthly data precision for each CEM from daily span checks; and
- Perform a quarterly accuracy assessment of each CEM.

The CEMs data accuracy is determined by either a relative accuracy audit (RAA), utilizing Reference Methods (RM) as specified in the Performance Specification Test (PST) or a cylinder gas audit (CGA) utilizing gases that have been certified by comparison to National Bureau of Standards (NBS) Gaseous Standard Reference Materials (SRMs) or NBS/EPA approved gas manufacturer's Certified Reference Materials (CRMs). If the inaccuracy exceeds 25 percent using the RAA or ± 15 percent using the CGA, the CEM is "out-of-control." At this time, the source must take corrective action to bring the system back into compliance.

The proposed rule was designed to assess the CEM's data precision and accuracy on an established frequency. If, through the audit evaluation, the data becomes questionable, then increased quality control quality improves to within acceptable limits. Consequently, the responsiblity of maintaining the CEM system within an acceptable range is solely upon the shoulders of the regulated facility.

Current regulations associated with continuous emission monitors require the source operator to perform a daily zero and span check of the monitoring system. The regulations are not specific under Subpart A of the General Revision of 40CFR60 as to whether this daily check is to be observed or recorded. The regulations do state, however, that if the daily zero and span check exceeds the applicable drift limits as specified in the Performance Specification, then the source operator must make appropriate adjustments to bring the continuous emission monitoring system within the drift specifications. This is the extent of quality assurance requirements associated with current regulations. Subpart A of the General Provision of 40CFR60 state:

> "...at all times, including periods of start-up, shutdown, and malfunction, owners and operators shall, to the extent practicable, maintain and operate only affected facility in a manner consistent with good air pollution control practice..."

Consequently, the present regulations lacks requirements for:

- Periodic assessment of CEMs data precision and accuracy;
- Requirements when CEMs corrective action must be taken; and
- Requirements for defining criteria for "unacceptable data."

Proposed Appendix F, Procedure 1, covers gas continuous emission monitors used to determine compliance with emission standards on a continuous basis. This would initially covered Subpart Da sources - Standards of Performance for Electric Utility Steam Generating Units for which construction is commenced after September 18, 1978. The proposed regulation does not apply to those Subpart of the regulations where CEM is used as a compliance test method, but is not used to show compliance on a continuous basis (i. e. smelters). The proposed regulation does not apply to sources where CEM is required for O&M purposes, rather than for compliance determination (i.e. NSPS Kraft pulp mills). The proposed regulation, consequently, would apply only to a very narrow population of the Subparts. This does not preclude, however, state and local agencies from implementing many sections of the proposed regulation on sources covered under the State Implementation Plans (SIP). Such regulatory vehicles as source permitting, consent decrees, variances etc. have been used successfully in the past by state and local regulatory agencies in implementing quality assurance requirements on regulated facilities.

The proposed regulation is divided into three major areas of concern associated with installed continuous emission monitors. They are:

- Quality control activities;
- Quality assurance activities; and
- Reporting requirements.

11.2.1 Quality Control (QC)

Quality control involves "those activities which will provide a quality product." Appendix F, Procedure 1 addresses this by requiring sources to develop a source specific quality assurance/quality control program including written procedures for continuous emission monitoring systems. Those activities which should be addressed in the QA/QC program are:

- Calibration technique/frequency;
- Calibration drift determination and adjustment procedures;
- Preventive maintenance procedures;
- Data recording and reporting procedures; and
- Program of corrective action for malfunctions continuous emission monitors.

These written procedures are routinely part of a source quality assurance plan. The objective of a source quality assurance plan, involving both quality assurance and quality control, is to delineate the activities necessary to ensure that emission monitoring data are complete, representative, precise and accurate. The quality assurance plan provides the framework for implementing quality assurance and quality control activities. Quality control procedures ensures that the data required is precise and accurate within established limits and if found outside those limits, provides procedures for corrective action to bring the system back within limits.

11.2.2 Quality Assurance (QA)

Quality Assurance activities are addressed in routine assessment of CEM data involving instrument precision and accuracy.

Instrument precision is determined each calendar month using span drift data from daily span checks. Each monitor is challenged with a calibration standard of known concentration at a span level (50-100% of span valve) on a daily basis. The difference between the actual concentration of the calibration standard and the concentration indicated by the monitor is calculated daily by the following equation:

$$d_i = \frac{Y_i - X_i}{X_i}$$

d_i = ____________

Where: Y_i = monitor indicated concentration from the i-th precision checks; and

X_i = known concentration of the precision check reference used for the i-th precision check.

For each month, the monthly average percent difference ($\overline{d}_j$) and the standard deviation of the percent difference (S_j) is used to calculate the upper and lower 95 percent probability limit [(UPL) and (LPL)]. Mathematically, this can be represented by the following equation:

$$UPL = \overline{d}_j + 1.96\ S_j$$

$$LPL = \overline{d}_j - 1.96\ S_j$$

The UPL and LPL are reported on the quarterly Data Assessment Report (DAR).

As proposed, Appendix F, Procedure 1 assesses accuracy on a periodic basis, of an installed continuous emission monitor, by utilizing a relative accuracy audit (RAA) and a cylinder gas audit (CGA). The accuracy assessment is performed within the first two months of each calendar quarter.

The procedure for the RAA is the same as for the relative accuracy test described in the applicable performance specification test requirements, except fewer sets of measurements would be required. For Kraft pulp mills, this would involve Federal Reference Method 16 or Federal Reference Method 16A. The relative accuracy (RA) would be calculated by the following equation:

$$RA = \frac{|\overline{d}| + |CC|}{RM}$$

Where:

RA = Relative Accuracy, % average;

$|\overline{d}|$ = Absolute value of the mean difference between reference method and continuous emission monitor value over a series of tests;

$|CC|$ = Absolute value of the confidence coefficient at the 2.5 percent error;

$\overline{RM}$ = Average Reference Method value over a series of tests.

Every other calendar month, a cylinder gas audit (CGA) is performed on the installed continuous emission monitor in lieu of the RAA . The CGA is performed by challenging the monitor (both pollutant and diluent) with an audit gas of known concentration at two points, as illustrated in Table 11.1.

TABLE 11.1
CYLINDER GAS AUDIT VALUES

Audit Point	Audit Range		
	Pollutant Monitor	Diluent Monitor	
		CO_2	O_2
1	20 to 30% of Span valve	5 to 8%	4 to 6%
2	50 to 60% of Span valve	10 to 14%	8 to 12%

The monitor should be challenged at each point for a sufficient time to assure equilibrium of the monitoring system. As good practices would dictate, the gas should be introduced as close to the probe tip as possible and pass through all active components of the monitoring system. Once again, the monitor response is compared to the gas cylinder concentration to calculate a percent difference by the following equation:

$$d = \frac{Y_i - X_i}{X_i} \text{ X100}$$

Where:

d = % difference;
Y_i = monitor indicated concentration from the gas cylinder audit point; and
X_i = known concentration of the gas cylinder audit point.

Provisions are provided within proposed Appendix F, Procedure 1, addressing corrective action requirements for both span drift and quarterly relative accuracy audits. Corrective action is required if:

- o Span drift exceeds "twice" the applicable monitor drift limit for 5 consecutive span checks ...CEM is "out of control." If the CEM is "out of control", then:
  - (a) Take corrective action (C/A); and
  - (b) Within 2 weeks of C/A, audit CEMs with RAA or CGA
- o Inaccuracy from quarterly RAA exceeds 25% or CGA exceeds ± 10% ...CEMs is "out of control." If the CEM is "out of control", then:
  - (a) Take C/A: and
  - (b) Within 2 weeks of C/A, audit CEMs with RAA or CGA.

In addition, data is determined unacceptable if:

- o Data collected following "out of control" condition may not be used as part of minimum daily requirement: and
- o Any single day data when span drift exceeds 4 times the applicable monitor drift limit may not be used as part of minimum daily requirement.

11.2.3 Reporting

At the end of each quarter, the monitor precision probability limits for each calendar month and accuracy assessment results involving either a RAA or a CGA determination are reported. In addition, the proposed regulations require reporting of excessive span drift and inaccuracy determination along with corrective action taken to bring system back under control. This information is reported on a Data Assessment Report (DAR). An example format is given in Figure 11.2.

11.3 SOURCE QUALITY ASSURANCE PROGRAM

11.3.1 Introduction

The primary objective of a source quality assurance program for CEMs is to ensure that all data collected and reported are meaningful, precise and accurate within a stated acceptance criteria. The program should be strong enough to ensure strict adherence to all established procedural requirements, but flexible enough to allow continuing evaluation of its adequacy and effectiveness. The objectives, therefore, of a source quality assurance program are to:

- Provide routine performance of personnel and/or equipment;
- Provide for prompt detection and correction of conditions that contribute to the collection of poor quality data; and
- Collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

- Routine training and/or evaluation of operators:
- Routine monitoring of the variables and/or parameters which may have a significant effect on data quality;
- Development of techniques to detect defects;
- Development of methods written procedures to qualify data; and
- Action strategies to increase the level of precision in the reported data and/or to detect equipment defects or degradation.

After a QA plan is written and implemented, procedures within the plan should point out necessary corrective action which, in effect, revises the plan. This would provide an on-going corrective action system.

Figure 11.2
Data Assessment Report (DAR)
Continuous Emission Monitoring (CEM)
for
Total Reduced Sulfur (TRS)

Period Ending Date ____________________ Year ____________________

1.0 General Information
1.1 Company Name ____________________
1.2 Plant Name ____________________
1.3 Source Unit No. ____________________
1.4 Monitor Location ____________________
1.5 Monitor Type/Model No. ____________________
1.6 Monitor Serial No. ____________________

	1	2	3
2.0 Quality Assessment			
2.1 Precision (for each month in quarter)			
2.1.1 Month of Quarter			
2.1.2 95 Percent Probability Limit			
2.1.2.1 Upper (UPL)	______	______	______
2.1.2.2 Lower (LPL)	______	______	______
3.0 Accuracy (fill in either 3.1 or 3.2)			
3.1 Relative Accuracy Audit (RAA)			
3.1.1 Date of Audit	______	______	______
3.1.2 Reference Method (RM) Used	______	______	______
3.1.3 Average RM Value	______	______	______
3.1.4 Absolute Value of Mean Difference |d|	______	______	______
3.1.5 Absolute Value of Confidence Coefficient |CC|	______	______	______
3.1.6 Relative Accuracy (RA), percent	______	______	______

	Audit Point 1 (Low Conc.)	Audit Point 2 (High Conc.)
3.2 Cylinder Gas Audit (CGA)		
3.2.1 Date of Audit	______	______
3.2.2 Cylinder ID#	______	______
3.2.3 Cylinder Certification Date	______	______
3.2.4 Certification Method	______	______
3.2.5 Cylinder Concentration	______	______
3.2.6 Monitor Response	______	______
3.2.7 Difference, percent		

Data Assessment Report (continued)

4.0 Corrective Action
  4.1 Excessive Span Drift
    4.1.1 No. of Times Monitor was "Out-of-Control" ____________________
    4.1.2 Corrective Action Taken ____________________
    4.1.3 Results of Audit After Corrective Action ____________________
  4.2 Excessive Inaccuracy
    4.2.1 Corrective Action Taken ____________________
    4.2.2 Results of Audit After Corrective Action ____________________

5.0 Authority
  5.1 Name ____________________
  5.2 Title ____________________
  5.3 Address ____________________
  5.4 Telephone Number ____________________
  5.5 Signature ____________________

The development of a quality assurance program deals not only with daily zero/span checks, quarterly audit techniques on precision/accuracy, but also involves the development and implementation of four (4) general categories. They are:

1. Management;

2. Measurement;

3. Documentation; and

4. Statistics.

Management: The first step in developing a Quality Assessment/ Quality Control program is the development of a written policy stating the objectives of quality assurance as part of the management effort. In addition, administrative procedures applicable to all measurement systems must be developed. The quality assurance policy and objectives should be applicable to pending EPA regulatory quality assurance procedures. Quality assurance reports and quality assurance graphics addressing data quality of each CEM system should be routinely summarized for internal distribution by the QA coordinator. Cost related items should be reviewed and changes made to obtain high quality data for the least cost.

Measurement: The second quality assurance/quality control program development step is the preparation of a Quality Assessment document that illustrates step-by-step procedures for CEM system start-up and calibration, internal CEM QA checks (daily, weekly, monthly, etc.), performance audits, system audits, calibration standards certification, CEM certification, data validation, maintenance (non-routine and scheduled) and intralaboratory quality assessment activities. Appendix F, Procedure 1 QA activities should be an integral part of the QA document.

Documentation: A document control system should be an integral part of the quality assurance plan. This involves proper identification and noted revisions of all quality assurance documents associated with the CEM system. All log books should be numbered and identified as part of the document control system. Users should maintain the following log books to document all QA/QC activities associated with the CEM system.

- Monitor Log Book;
- Procurement Log Book;
- Calibration Standards Log Book;
- Laboratory Log Book;
- Excess Emission Log Book;
- Daily Monitor Log Book; and
- Periodic Audit Log Book.

The document control system should also maintain records on all monitoring equipment (manufacturer's serial number, location), spare parts inventory, all components and their status (repair shop, manufacturer or discarded) and QA audit standards (NBS traceable, recertified date). A document distribution system should be established in order to provide the latest written procedures to all concerned personnel.

Statistics: The statistics category includes the tasks of data reduction and calculation in order to express the data in units of applicable standard. Statistics are essential to any adequate quality assurance program because they provide information concerning monitor performance (short and long term) and data validity. Corrective action begins with statistical evaluation.

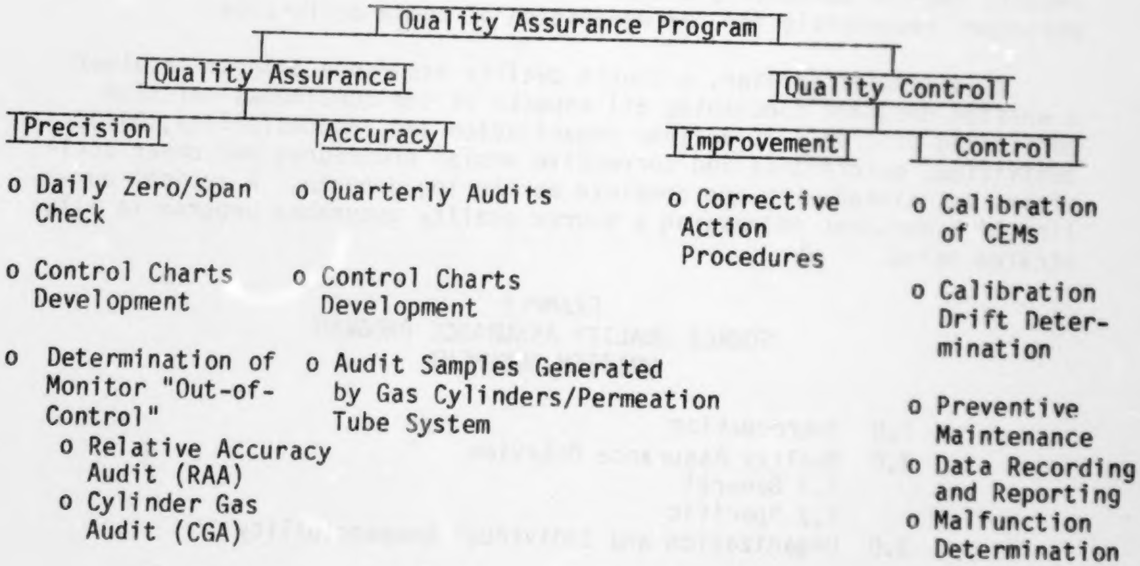
From the statistical evaluation of the monitoring data, charts can be developed. These charts are used to detect long term trends and establish "out of control" criteria limits. Confidence limits are identified on the control chart so that future data values can be plotted to detect any significant changes from past performance.

11.3.2 Source Quality Assurance Program

A source specific quality assurance program can be divided into two major functional groups:

- Quality Assurance
- Quality Control

Quality control has historically been defined as "those activities which will provide a quality product", whereas quality assurance is "the system of activities to provide assurance that the quality control program is performing adequately." Quality control involves routine checks included in normal internal procedures. Quality assurance may be viewed as "external" quality control involving system audits, statistical evaluations and other functions which are outside the normal routine functions. Figure 7.3 illustrates the different activities associated with each major functional group.



Quality Assurance Program
Quality Assurance
Quality Control
Precision
Accuracy
Improvement
Control
o Daily Zero/Span Check
o Control Charts Development
o Determination of Monitor "Out-of-Control"
o Relative Accuracy Audit (RAA)
o Cylinder Gas Audit (CGA)
o Quarterly Audits
o Control Charts Development
o Audit Samples Generated by Gas Cylinders/Permeation Tube System
o Corrective Action Procedures
o Calibration of CEMs
o Calibration Drift Determination
o Preventive Maintenance
o Data Recording and Reporting
o Malfunction Determination

Figure 11.3. Source Specific Quality Assurance Program

The purpose of developing and implementing a source quality assurance (QA) plan is: (1) to assure acceptable precise CEM data quality, and (2) to assure acceptable CEM data recovery and system operating availability. The draft version of EPA's Appendix F to 40 CFR 60, provides an outline of requirements for CEM Quality Assessment Plans for facilities operating monitors as compliance measurement methods. Appendix F requirements not only define data precision, accuracy, and system availability goals, but also specify that comprehensive operation and maintenance (Q&M) and quality assurance/quality control (QA/QC) audits and measurements be conducted. The requirements further stipulate corrective action and alternative measurement methods when the QA/QC checks indicate that the QA and availability goals are not achieved. A QC program defining calibration, maintenance, and corrective action must also be developed.

Consequently, the requirements of Appendix F dictate documentation of all phases of a company's QA Plan. Included are all QA/QC, Q&M, and recordkeeping activities. The QA Plan should also address other activities such as certification testing, QA Plan organization, and personnel responsibilities. A standard operating procedures (SOP) manual defining all activities, responsibilities, communication, and documentation procedures should be developed to serve as the working reference of the QA Plan.

Following is a discussion of a typical QA Plan applicable to monitoring total reduced sulfur (TRS) from Kraft pulp mills incorporates all the requirements of Appendix F. The QC program defines and documents the O&M (preventative and repair) procedures. Additional elements of the plan described in this chapter include an organization plan which identifies the responsibilities for QA Plan activities and distribution recording of results. The QA Plan should identify when the O&M and QA/QC activity results require corrective action or alternative monitoring methods, and personnel responsible for implementation of these activities.

As discussed earlier, a source quality assurance program involves a written document containing all aspects of the continuous emission monitoring program. It defines organization and responsibility, QA/QC activities, maintenance and corrective action procedures and other activities associated with the complete monitoring program. A typical outline of a document addressing a source quality assurance program is illustrated below.

EXAMPLE
SOURCE QUALITY ASSURANCE PROGRAM
WRITTEN DOCUMENT

1.0 Introduction
2.0 Quality Assurance Overview
    2.1 General
    2.2 Specific
3.0 Organization and Individual Responsibility

- 3.1 Personnel Assignments and Responsibilities
    - 3.1.1 Organization
    - 3.1.2 Program Management
    - 3.1.3 Field Operations
    - 3.1.4 Laboratory Operations
    - 3.1.5 Data Management
- 3.2 QA Responsibilities
    - 3.2.1 Quality Assurance Coordinator
    - 3.2.2 Field Personnel

4.0 Quality Assurance/Quality Control
- 4.1 Quality Assurance
    - 4.1.1 Activities
    - 4.1.2 Personnel Responsibilities
- 4.2 Quality Control
    - 4.2.2 Activities/Corrective Action
    - 4.2.1 Recordkeeping

5.0 Data Handling, Validation and Reporting
- 5.1 Data Logistics
- 5.2 Data Handling and Statistical Analysis
- 5.3 Control Charts
- 5.4 Data Validation Criteria
- 5.5 Data Reporting
- 5.6 Data Forms

6.0 Operation and Maintenance Program
- 6.1 General
- 6.2 Preventive Maintenance
- 6.3 Corrective Maintenance
- 6.4 Spare Parts Inventory
- 6.5 Maintenance Documentation

7.0 Quality Assurance Audits
- 7.1 Self Auditing
- 7.2 Corporate Auditing

8.0 Recordkeeping and Reporting Requirements

11.3.2.1 Introduction -

The introduction should contain language affirming corporate policy to operate and maintain its facilities in strict adherence to all applicable environmental rules and regulations. Likewise, a committment to obtaining all data to demonstrate necessary activities dealing with the continuous emission monitoring system are being performed to ensure that all environmental measurements are of high quality.

11.3.2.2 Quality Assurance Overview -

Quality Assurance depends on the completion of all activities stated in the quality assurance document. The objective of the quality assurance document is to delineate those activities necessary to ensure that emission monitoring data are complete, representative and of determined precision and accuracy. The document addresses activities as responsible individuals, data integrity, documentation, training programs and corrective action activities.

11.3.2.3 Organization and Individual Responsibility -

Historically, the management of quality assurance programs have incorporated, at a minimum, three organizational levels. Level I, Manager of Environmental Engineering, is responsible for the implementation of and continued support to the QA program. Company QA policy, administrative support, local assistance, development of strategies, system analysis, promulgation of permit requirements and interface between source and regulatory agencies are some of the other functions of Level I.

Level II, Quality Assurance Coordinator, is responsible for the implementation of the quality assurance program. The Quality Assurance (QA) Coordinator develops and carriers out the Quality Control Programs, including statistical procedures and techniques, which will help the source meet agency requirements. In addition, the QA coordinator schedules and performs non-routine audits and quarterly audits, evaluates new QA procedures for applicability, evaluates data quality and maintains related quality control charts and records. It is the QA coordinator's responsibility to respond to quality control problems and coordinate those activities with Level I. In addition, the QA coordinator should prepare monthly and quarterly reports to summarize:

- Reliablility of the CEM system and its components;
- Quality of data generated;
- CEM problem areas;
- Corrective actions taken and their results; and
- Quarterly excess emission reports.

This information is then submitted to Level I, Manager of Environmental Engineering, for approval and distribution.

Level III involves the CEM operator who ensures that good quality data is obtained from the CEM system.

Daily quality assurance zero/span checks with associated documentation, preventative maintenance procedures, sample collection, and data reporting all fall within the responsiblity of the CEM operator.

Table 7.2 summarizes the quality assurance elements associated with each level of responsibility.

TABLE 11.2
RESPONSIBILITIES OF LEVELS I, II, AND III IN A SOURCE QA/QC PROGRAM

Level I and Level II	Level II and III	Level III
Supervisor & QA Coordinator	Supervisor & Operator	Operator
o Document Control/ Revisions; o QA Policy & Objective; o Organization; o Quality Planning; o Training; o Quality Cost; o Interlaboratory Testing; o Audit Procedures; o Data Validation; and o Quality Reports to Management.	o Corrective Action; and o Procurement Quality Control;	o Preventive Maintenance; o Data Reporting; o Calibration; and o Document Control.

A table should be established identifying CEMs program participants, name, title, address and telephone number along with responsibilities. An example is given in Table 11.3.

A key element to the successful implementation of the CEM QA Plan is the organization of personnel and activities. The SOP manual should define all QA/QC, maintenance, data reduction, documentation (record-keeping), and communication activity responsibilities and identify the personnel (by job category and by name) assigned each of these responsibilities.

A matrix of all personnel and activities associated with each major element of the plan (Q&M, QA/QC, data reduction) shall be prepared. Within this matrix, each individual activity should have associated documentation and communication responsibility defining what information is to be documented, where it will be filed, and who must be informed, verbally or in writing, of the results of the activity.

The mechanisms which initiate each activity should be identified within the matrix as scheduled as well as within the malfunction mechanisms. The frequency of scheduled activities such as preventative maintenance and QA audits should be specified. Malfunction initiated activities such as repair maintenance, QA audits following maintenance, and operating alternative measurement methods should be ordered or requested. The requesting person or organization should be specified within the matrix.

In addition, flow charts should be constructed indicating "flow" of information between individuals within the CEM program. An example of a "typical" flow chart is given in Figure 11.4.

TABLE 11.3
CLEAN PAPER COMPANY
SOURCE QUALITY ASSURANCE PROGRAM
PROGRAM PARTICIPANTS AND RESPONSIBILITIES

Level	CEM Program Participant	Name, Title, Address Telephone No.	Responsibility
I_1	Plant Manager	Mr. Bob Timson Clean Paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 923)	o Responsible for total plant operation;
I_2	Plant Operations Supervisor	Mr. Jim Limb Clean Paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 813)	o Data review and verification; o Maintain compliance status (modify operations if necessary);
I_3	Environmental Engineering	Mr. Jerry Figure Clean Paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 714)	o Ensures compliance with environmental regulations; o Directs activities over engineering department, including implementation of QA program;

TABLE 11.3 (continued)
CLEAN PAPER COMPANY
SOURCE QUALITY ASSURANCE PROGRAM
PROGRAM PARTICIPANTS AND RESPONSIBILITIES

II$_1$	CEM Supervisor	Mr. Tom Electron Clean Paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 622)	o Responsible for all operation and maintenance activities for installed CEMs; o Responsible for implementation of the QAS Program; o May also be responsible for Quality Assurance activities;
II$_2$	CEM-QA Coordinator	Mr. Pete Exact Clean Paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 561)	o Responsible for all QA source activities associated with the CEM program; o Implements and performs weekly, monthly, and quarterly QA checks;
III	CEM Instrument Specialist	Mr. Scott Work Clean paper Company Pine Bluff, North Carolina (919) 877-3611 (ext. 400)	o CEMs maintenance and calibration; o Maintain instrument logs; o Report instrument problems.

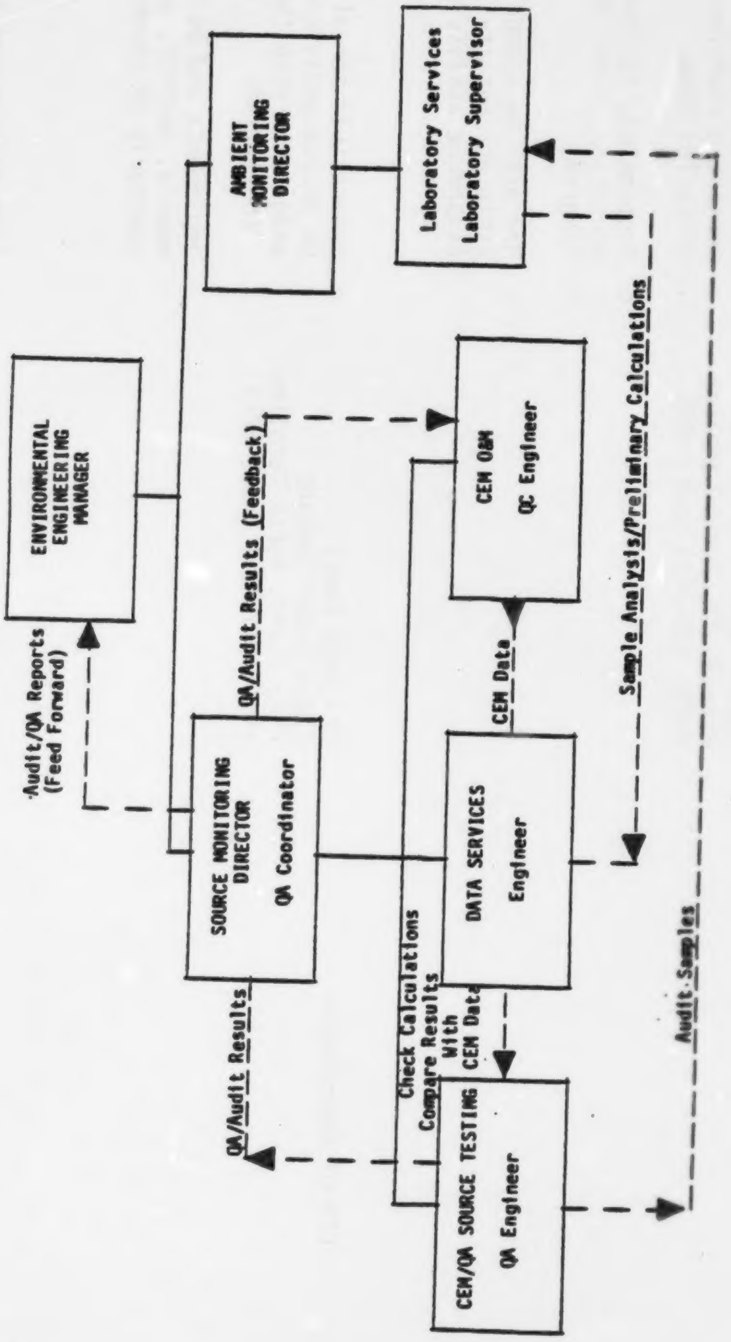

ENVIRONMENTAL ENGINEERING MANAGER
AMBIENT MONITORING DIRECTOR
Laboratory Services Laboratory Supervisor
Audit/QA Reports (Feed Forward)
QA/Audit Results (Feedback)
CEM O&M QC Engineer
SOURCE MONITORING DIRECTOR QA Coordinator
CEM Data
Sample Analysis/Preliminary Calculations
DATA SERVICES Engineer
QA/Audit Results
Check Calculations Compare Results With CEM Data
CEM/QA SOURCE TESTING QA Engineer
Audit Samples

Figure 11.4. Personnel Flow Chart Within Source QA Program

TABLE 11.4
QA/QC ACTIVITIES ASSOCIATED WITH MONITOR PRECISION AND ACCURACY

QA/QC Activities	Purpose	Limits	Corrective Action
Relative Accuracy	Assess relative accuracy	± 20%	1. CEM O&M group repairs as required. 2. CEM Data Services evaluates effect on data. 3. CEM QA group performs repeat audit (RAA) after corrective action.
Cylinder Gas Check -1 (Single Point)	Assess calibration error Assess response time	+ 5% T5 minutes	1. CEM O&M group repairs as required. 2. CEM Data Services evlauates effect on data. 3. CEM QA group performs repeat audit (CGA-1) after corrective action.
Cylinder Gas Check -2 (Multipoint)	Assess precision Assess calibration error	+ 5% ± 5%	1. CEM O&M group repairs as required. 2. CEM Data Services evaluates effect on data. 3. CEM QA group performs repeat audit (CGA-1) after corrective action.
System Appraisal	Assess Calibration error	± 5%	1. CEM O&M group repairs as required. 2. CEM Data Services evaluates effect on data. 3. CEM QA group performs repeat audit after corrective action.
Walkthrough Check	Assess general condition of gas monitoring systems	No readily apparent problems	1. CEM QA Coordinator establishes need for and implements appropriate correction action. 2. CEM QA Coordinator may initiate another appropriate audit.

11.3.2.4 Quality Assurance/Quality Control

As illustrated in Figure 7.3, quality assurance/quality control functions are performed to enable the source to determine the precision and accuracy of an installed CEM system. This may involve a simple walkthrough check, observing gauges etc. or it may involve a complete relative accuracy check. The performance of each activity enables the source operator to evaluate the system and, if need be, perform a higher level of QA/QC checks if deficiencies are note. Table 7.4 lists the various QA/QC activities involving monitor precision and accuracy.

The walkthrough and system appraisal check are the least time consuming functions of a source QA/QC program. Gauges, valves, temperature settings etc. are recorded on the daily checklist and compared to "baseline" values. The general condition of the CEM system is assessed and compared to historical data. If deficiencies are observed, appropriate action is taken.

The most common QA/QC activity performed on a source CEM system is the daily zero/span check. The daily zero/span check allows the operator to challenge the monitor with a known concentration of gas and observe the monitor response.

The results of the daily zero/span calibration check should be recorded on the daily checklist. The calibration check is an excellent indicator of its proper operation. The individual performing the daily maintenance should be aware of the system operation as demonstrated by the calibration checks. Maintenance performed without reviewing the instrument response to daily calibration is only partially effective. As daily calibration values are recorded, trends develop and the maintenance technician becomes familiar with the expected operating parameters for the day. Results outside those expected operating parameters should indicate not only the problem but the probable cause of that problem. The daily calibration values provide a starting point for troubleshooting wherever a problem is indicated.

From the zero and span checks, control limits can be calculated (95% probability limits) and recorded on a monitor-specific control chart, as illustrated in Figure 11.5.

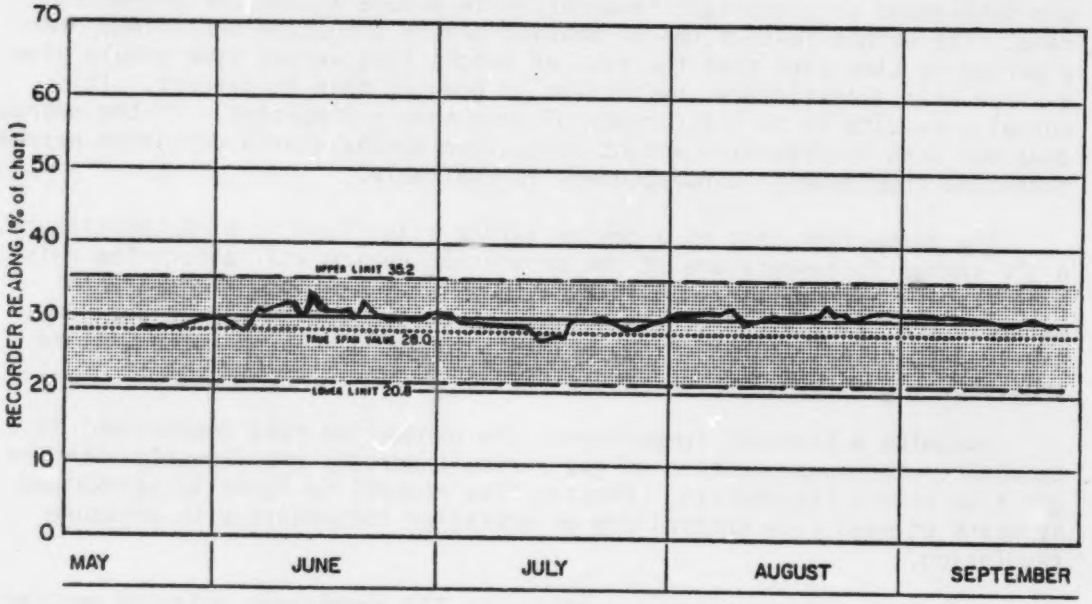


Figure 11.5. Control Chart for Daily Zero/Span Checks

As discussed in Appendix F, when the limits have been exceeded, a multipoint calibration, using span gases should be initiated. The procedures/data forms used in the multipoint check should be part of the Standard Operating Procedure (SOP) Manual.

Each CEMS analyzer must be calibrated at least every 24 hours. Currently, the only two options for calibrating a TRS CEM system are gravimetrically certified permeation devices and cylinders of TRS that have been analyzed. The accuracy of those two methods of calibration will reflect directly upon the accuracy of the data generated, and have been discussed fully in Chapter 6.0.

If the calibration is performed by permeation devices, a number of parameters are important to the accuracy of calibration. One of the most important is the determination of the emission rate of the permeation device. The weight loss is normally determined by weighing the devices routinely for a period of four to six weeks, during which time the devices are maintained at a constant temperature to ensure a constant permeation rate. The weight loss of the permeation device should be determined over a period of time such that the plot of weight loss versus time should give a slope with a confidence coefficient of greater than 95 percent. This normally results in an inaccuraacy of less than ± 2 percent. If the source does not wish to determine weight loss, then purchase of a certified permeation tube from several manufacturers is available.

The permeation rate of a device varies significantly with temperature. A 1°C change in temperature of the permeation device will affect the emission rate by approximately 10 percent. It is, therefore, necessary to maintain the temperature of the permeation device during use at the same temperature of calibration (± 0.1°C) to ensure the emission rate will be constant (± 2 percent) under normal circumstances.

Assuming a constant temperature, the permeation rate (mass/time) is constant. The concentration of gas varies inversely and linearly with the gas flow across the devices. Precise flow control is normally maintained by means of mass flow controllers or precision rotameters with pressure regulation.

The most common method of calibrating TRS continuous emission monitoring systems is the use of hydrogen sulfide in nitrogen. The concentration of H_2S in nitrogen should be in the range of the analyzer (approximately 80 percent of span) or a higher concentration that requires dilution before use. Most commonly, a high concentration cylinder (1,500 to 3,000 ppm) is purchased and diluted approximately 100 fold for daily calibration. The advantage of using a high concentration gas is that only a small amount is required to calibrate the system and the gas will last much longer. The disadvantages of using a high concentration gas is that an accurate dilution system is required to continually provide the same dilution. When high concentration gases are used, not only must the user be concerned with the accuracy of the concentration in the cylinder, but also the accuracy of the dilution.

11.3.2.5 Data Validation and Reporting -

Criteria for data invalidation have been addressed in drafts of Appendix F - Procedure 1, Quality Assurance Requirements for gas CEM's, and it is likely that some version of these criteria will be retained when Appendix F is promulgated in its final form. If this proves to be the case, invalid data will be defined in relation to two monitor conditions:

(1) Breakdown; and
(2) "Out of Control".

Excessive span drifts and excessive errors in relative accuracy are cited as causes of monitor breakdown and out of control. Accordingly, the quality assurance plan should provide for identification of these criteria.

Many monitors and data recording systems incorporate aids to data validation such as flagging operational parameters and monitor calibrations which are outside acceptable limits. The CEM operator should check all flagged items daily for reasonableness and communicate with the quality assurance coordinator on questionable items.

Control charts for monitor calibration should validate monitor pollutant results and should be checked weekly by the QA coordinator.

To validate the Data Acquisition System (DAS) calculations of results, 10% of the first month's strip chart monitor data should be reviewed and evaluated. If the results compare within 3% of the DAS, the DAS should be considered correct. On a continuing basis, 5% to 10% of the overall data output of each CEM system should be evaluated in this manner.

11.3.2.6 Operation and Maintenance Program -

A comprehensive operation and maintenance (O&M) program coupled with routine quality assurance (QA) checks are vital elements of a successful CEM program. They provide the necessary documentation to evaluate the precision, accuracy and representativeness of the source measurement system. The gathering and processing of invalid data is historically coupled with improper operation and/or lack of maintenance of CEM systems. This, in turn, leads to excessive monitor downtime. Under many Subparts of 40CFR60, a specified minimum data capture is required. Consequently, a well documented O&M/QC program serves both industry and regulatory agencies.

The appropriate procedures for a O&M/QC program are monitor-specific and site-specific. The program should include the following basic elements:

- Documentation of instrument system operating parameters using standardized forms and control charts;
- Daily zero and span calibration checks for confirming that the instrument calibrations are maintained within control limits;
- Validation of data reduction process from raw data collection through reporting;

- Determination of the accuracy and precision of collected data;
- Performance of quarterly independent audits; and
- Periodic maintenance procedures and practices.

Appropriate quality assurance checks must be monitor specific and source specific. Documentation should involve a step-by-step approach to the daily quality assurance checks with instructions for action to be taken if the appropriate response is not obtained. At a minimum, routine quality assurance checks should address the following topics:

- Set of procedures for monitor specific daily zero/span function;
- Guidance for corrective action;
- Control charts; and
- Documentation involving monitor log book for routine entry and routine/major maintenance entries.

Figure 11.6 illustrates a typical source specific troubleshooting guide, while Figure 11.7 illustrates a source trouble report/work request form.

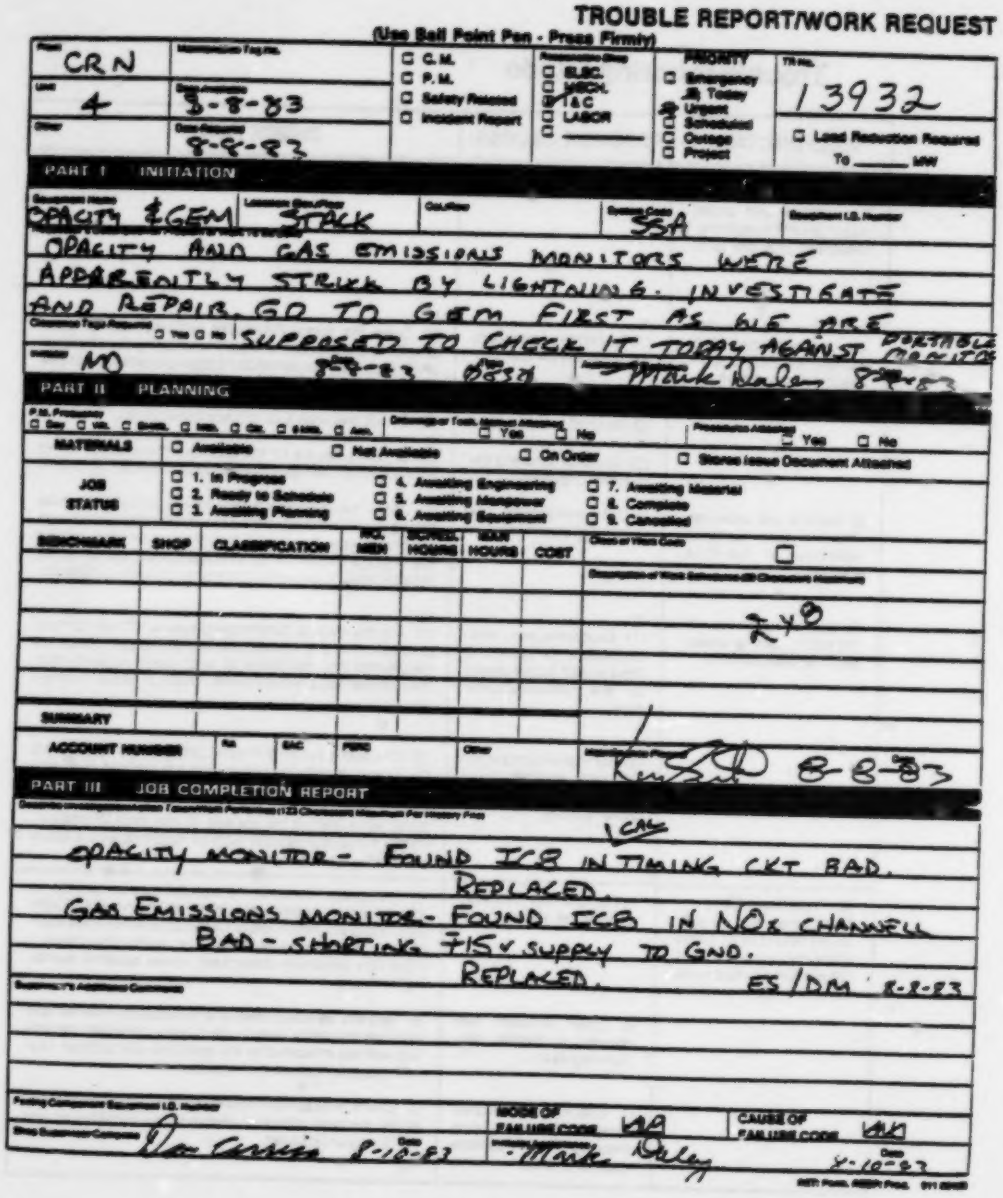
The same individual who performs the daily zero/span checks should be responsible for routine adjustments to the monitoring system when discrepancies are noted. Long-term monitor performance should determine the appropriate frequency of various QC activities. Adequate records must be maintained to document these activities.

It is essential to develop monitor and site specific instructions for the routine quality assurance activities required by both manufacturer and Appendix F to ensure proper operation of the CEM system. Quality assurance activities of zero/span checks are to be performed daily, as specified in the Standard Operational Procedure Manual (SOP).

Troubleshooting Guide

MALFUNCTION	POSSIBLE CAUSES	CHECK FOR
1. No Output Signal The control unit panel meter and/or peripheral recorders indicate zero		
A. Control unit indicates an unsuppressed dark current on the 10 ppm range of 0.3 to 5 ppm.	A. (1) No sample gas reaching the analyzer unit.	A. (1) Does the panel flowmeter indicate that at least .5 scfh, and preferably 2.0 scfh, is entering the analyzer unit? If not, make external correction and provide sample gas to the instrument.
	(2) Blocked sample capillary.	(2) Check and unplug or replace as required.
	(3) No ozone reaching the reaction chamber.	(3) Is the O_2 source for the ozonator connected? Is the ozonator high voltage power supply working properly?
B. Control unit does not indicate any upscale deflection in full-scale position.	B. Defective amplifier or ± 15 V DC power supply.	B. Check the DC power supply for the amplifier by measuring the DC voltage applied to the amplifier underneath the control unit. To each terminal from the center ground the voltage should be ± 15 volts. Check the amplifier itself by replacing it with a spare and noting the difference.
C. Control unit does not indicate any unsuppressed dark current.	C. (1) Disconnected, misconnected or defective input and/or output cables to the photomultiplier tube.	C. (1) Are the cables connected properly? If not, correct problem. Are the cables themselves okay? Check by measuring the resistance of each cable to verify that the resistances are not infinite. Replace cable if necessary.
	(2) Defective photomultiplier base, photomultiplier tube or PM high voltage power supply.	(2) Check the output of the photomultiplier high voltage DC power supply by measuring the voltage between ground and the center post of the PMHV connector terminal inside the rear of the control unit back panel. 1600-2000 volts should be applied to the photomultiplier. Check the photomultiplier tube by replacing with a spare and noting any difference.
2. Flow Sensitivity Small variations (± 1 scfh) in the flow rate of a constant concentration sample produce output variations of several percent.	A. Sample leak, probably outside the analyzer unit.	A. If possible, connect the sample source directly to the instrument bypassing external plumbing. (CAUTION: Do not bypass cold traps or particulate filters if the sample contains excessive moister or particulate matter.) If the flow sensitivity disappears, check external plumbing for leaks.
	B. Leak through diaphragm of sample vacuum regulator.	B. Vary the sample pressure at the source. If the sample vacuum regulator fails to maintain a constant sample vacuum (as indicated by the analyzer unit sample vacuum gauge), replace the regulator
	C. Cracked or chipped sample capillary or O-ring missing from sample capillary holder.	C. Check the capillary holder in the sample line leading to the reaction chamber. Replace the capillary or add the O-ring as required.

Figure 11.6. Source Specific Troubleshooting Guide.



TROUBLE REPORT/WORK REQUEST
(Use Ball Point Pen - Press Firmly)

CRN
4
8-8-83
8-8-83

☐ C.M.
☐ P.M.
☐ Safety Related
☐ Incident Report

☐ ELEC.
☐ MECH.
☑ I&C
☐ LABOR
☐ ____

PRIORITY
☐ Emergency
☐ Today
☑ Urgent
☐ Scheduled
☐ Outage
☐ Project

13932

☐ Load Reduction Required
To ______ MW

PART I INITIATION

OPACITY & GEM | STACK | SSA

OPACITY AND GAS EMISSIONS MONITORS WERE APPARENTLY STRUCK BY LIGHTNING. INVESTIGATE AND REPAIR. GO TO GEM FIRST AS WE ARE SUPPOSED TO CHECK IT TODAY AGAINST PORTABLE MONITORS

☐ Yes ☐ No

NO
8-8-83 0830
Mark Daley 8-8-83

PART II PLANNING

☐ Yes ☐ No

☐ Yes ☐ No

MATERIALS ☐ Available ☐ Not Available ☐ On Order ☐ Stores Issue Document Attached

JOB STATUS
☐ 1. In Progress
☐ 2. Ready to Schedule
☐ 3. Awaiting Planning
☐ 4. Awaiting Engineering
☐ 5. Awaiting Manpower
☐ 6. Awaiting Equipment
☐ 7. Awaiting Material
☐ 8. Complete
☐ 9. Cancelled

BENCHMARK	SHOP	CLASSIFICATION	NO. MEN	SCHED. HOURS	MAN HOURS	COST
SUMMARY						

☐

2×8

ACCOUNT NUMBER

8-8-83

PART III JOB COMPLETION REPORT

OPACITY MONITOR - FOUND IC8 IN TIMING CKT BAD. REPLACED. (CAL)

GAS EMISSIONS MONITOR - FOUND IC8 IN NOx CHANNELL BAD - SHORTING ∓15v SUPPLY TO GND. REPLACED.

ES/DM 8-8-83

MODE OF FAILURE CODE [illegible]
CAUSE OF FAILURE CODE [illegible]

8-10-83
Mark Daley
8-10-83

Figure 11.7. Source Trouble Report/Work Request

11.3.2.6.1 Routine Maintenance -

Periodic checks of the CEMS and its operation are mandatory. Even though a system may provide excellent quality data initally, without routine maintenance and system checks, the quality of the data will undoubtedly degenerate with time.

Maintenance checklists are one of the tools management can use to ensure that the proper preventive maintenance is being completed. The checklist should provide a place to record all settings and indicators of proper operation, indicate the items to be checked and provide a place to document repairs and replacement of parts. The checklist should list daily, weekly and monthly checks of various maintenance items, and it should be system specific because each system will require slightly different gauge settings and meter readings for proper operation. The proper recording of maintenance items provides a history to correlate outages and potential problem areas. Table 7.5 illustrates an example of a source QA maintenance timetable.

11.3.2.6.2 Preventive Maintenance -

The Operation and Maintenance section of a quality assurance program should contain the following:

- A concise, simplified trouble shooting guide and diagnostic chart to assist operators in identifying monitor problems;
- Established verbal and written lines of communication to assure prompt notification to maintenance, physical plant and environmental management of monitor operating problems;
- A maintenance request form with routing priority assignment, and job completion follow-up and failing to assure management awareness of monitor operational status.
- An on-going training program to ensure that the maintenance staff is technically capable of instrument repair;
- Develop a spare parts inventory and stock replenishment program based on suppliers' recommendations and available information on likely modes of failure; and
- Review major repair and parts supply services available from vendors, parts distributors, repair centers, etc. and implement the best available.

Table 11.6 illustrates a CEM preventative maintenance guide.

11.3.2.7 Quality Assurance Audits -

Quality assurance audits are independent checks made by the auditor to evaluate the quality of data generated by the total monitoring system (sample collection, sample analysis and data processing). These audits are performed independent from and in addition to normal quality control

TABLE 11.5
SOURCE QUALITY ASSURANCE PROGRAM
TOTAL REDUCED SULFUR
MAINTENANCE TIMETABLE

Activity/Checks	Frequency					
	Daily	Weekly	Monthly	Quarterly	Semi-Annually	Annually
Calibration System Check	X					
Permeation Bath Temperature Check	X					
Strip Chart Paper Check/Inking	X					
Printer Paper and CRT check	X					
Hoses, Gauges and Valves	X					
Flowmenter Checks	X					
SO_2 Scrubber Check	X					
Oxidixing Cell and Sample Line Heat Check	X		X			
Sample Line Pressure	X					
GC Oven Temperature	X					
Calibration Gas Pressure/Flowrates		X				
Permeation Tube		X				
Sample Gas Flow Rates		X				
Condenser Water Temperature		X				
Analyzer/Dilution Air Check		X				
Data Processor Maintenance		X				
Sample Dew Point		X				
Voltage Checks			X			
Service Sample/Purge Pump			X			
Vaporizer Filter			X			
Probe Inertial Filter			X			
Charcoal in Clean Air Supply			X			
Replace Filters				X		
Vacuum Pump Oil				X		
Vacuum Pump Diaphragms				X		
Vacuum Pump Disc Valves and Gaskets				X		
Sample Interface Enclosure				X		
Gas Connections				X		
Sample Transport Lines				X		
Recorder Maintenance	X			X		X
Zero Air System Check			X		X	

TABLE 11.6
EXAMPLE RECOMMENDED PREVENTATIVE MAINTENANCE SCHEDULE
STI TRS CEM SYSTEM

```
                   07:30:15   JULY  1  1984
         RECOMMENDED PREVENTATIVE MAINTENANCE SCHEDULE

                                                       VALUE/CHECK  INITIALS
DAILY

1.   Check Oxidizer temperature - 1500 F +/- 50        -----------  --------
2.   Check Dilution Control pressure gauges:
a.   Sample pressure - 20 PSIG                         -----------  --------
b.   Dilution air pressure - 30 PSIG                   -----------  --------
c.   Calibration gas pressure - 30 PSIG                -----------  --------
d.   Calibration dilution air pressure - 30 PSIG       -----------  --------
3.   Check sample bypass flow meter - 1.5 l/min        -----------  --------
4.   Liquid level in SO2 scrubber water reservoir.
Fill within one half inch of top.                      -----------  --------
5.   Check SO2 backflush pressure gauge - 30 PSIG      -----------  --------
6.   Check air dryer indicator column - deep blue      -----------  --------
7.   Check air dryer outlet pressure - 60 PSIG         -----------  --------
8.   Check sample pump outlet pressure - 30 PSIG       -----------  --------
9.   Check steam pressure gauge at probe - 25 PSIG     -----------  --------
10.  Check sweep air pressure in probe box - 10 PSIG   -----------  --------
11.  Check calibration report - within limits          -----------  --------
12.  Check printer paper                               -----------  --------

Weekly

1.   Check sample Dewpoint at bypass flowmeter vent.  (Sample dewpoint
will be approx. 10 degrees F. greater than the dewpoint of the inst.
air)  Maintenance on the Sampling or Dry air systems is indicated if
the sample dewpoint is greater than -15 degree F.      -----------  --------
2.   Check calibration gas cylinder pressure.  The H2S cylinder must be
replaced when the pressure is below 300 PSIG           -----------  --------

Monthly

1.   Change the vaporizer filter                       -----------  --------
2.   Change the inertial filter                        -----------  --------
3.   Clean the probe eductor                           -----------  --------
4.   Repack the SO2 Scribber columns                   -----------  --------
5.   Check the calibration gas flow rates and enter the new computed value
into the computer                                      -----------  --------
6.   Visual inspection of the Probe/Conditioner Ass.   -----------  --------

Quarterly

1.   Change sample pump diaphragms                     -----------  --------
2.   Change sample pump disc valves and gasket         -----------  --------
3.   Change 'O' ring seals on probe barrel connectors  -----------  --------
```

---

[a] This preventive maintenance schedule may not apply to all TRS CEM systems.

checks by the system operator. They provide an independent means for determining the precision of the reported data, the adequacy of the monitoring operation and maintenance procedures, and the effectiveness of the quality control system. Both announced and unannounced audits should be scheduled. The audits provide a routine quality control check on the monitoring system and a quantitative performance evaluation to determine compliance with monitoring regulations and emission limitations.

11.3.2.7 1 Dynamic Audit -

Proposed Appendix F, Procedure 1, specifies relative accuracy audits every other quarter and cylinder gas audits quarterly. Specific gas concentrations are specified with appropriate actions required if excessive inaccuracy occurs. Quarterly audits are conducted in order to assess the accuracy of the CEMs in accordance with the provisions of Appendix F, Procedure 1. The CEMs should be audited at two audit points according to the following schedule:

Audit Point	Audit Range Pollutant Monitor	Diluent Monitor CO_2	 O_2
1	20 to 30% of monitor calibration full scale	5 to 8% by volume	4 to 6% by volume
2	50 to 60% of monitor calibration full scale	10 to 14% by volume	8 to 12% by volume

Only audit gases that have been certified by comparison to National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRMs) or use of gases that have been certified by EPA Traceability Protocol No. 1 should be used as part of the quarterly audit program.

The performance audit procedures are monitor specific to qualify and quantify the validity of the CEM system. For the gas cylinder audit, the percent difference is calculated and reported by the Quality Assurance Coordinator to the Manager, Environmental Engineering.

For the Relative Accuracy Audit (RAA), the relative accuracy is determined by adding the absolute value of the mean difference between the monitor and the reference method plus the 2.5% error confidence coefficient divided by the Reference Method.

11.3.2.7.2 Federal Reference Method 16 -

Federal Reference Method 16 can be used as a quality assurance check. Quality control as specified in EPA Method 16 should be followed. Gravimetrically certified permeation devices should be used to calibrate the GC before and after each three hours of testing. The permeation tube devices should be housed in a constant temperature bath whose temperature is certified to ±1°C with reference to an NBS traceable standard. The gas flow across the devices should be measured each time of use with a soap bubble flow tube.

The recovery of H_2S through the TRS sampling and analysis system should be determined before and after each three hours of sampling. If the loss of H_2S through the system exceeds 20 percent, the data should be invalidated. For system losses of 20 percent or less, the data from the source can be corrected by the mean recovery value obtained before and after the three hours of sampling.

Before beginning Reference Method 16, the span of each CEM should be adjusted to approximately 30 ppm H_2S. The gas used to calibrate the CEM should be analyzed with the GC using certified permeation devices as a reference. The concentration of the CEM calibration gas should be based on the GC results regardless of the concentration specified by the vendor.

The response of each CEM should be evaluated using a known concentration of H_2S. The sample should be injected at the probe and drawn through the complete sampling and analysis system. The response from the CEMS should be within ±5 percent of the known concentration.

Quality assurance testing should be completed in a stepwise fashion. If the analyzer appears to be operating incorrectly during any step, the problem should be identified and corrected before proceeding. Relative accuracy testing should be initiated only after all preliminarey quality control has been completed.

Gravimetrically certified permeation devices should be used as reference for the Referenced Method testing. One device for each compound should be obtained. Each device should be certified at a standard temperature by the vendor.

Calibration of the gas chromatograph for the reference method testing before and after each three hours of analyses should be performed. An H_2S recovery check on the system before and after each three hour and after each run is also important. If the minimum recovery specified by EPA Method 16 is not met, discarding the data as invalid is appropriate. If the minimum system recovery is obtained, then one should correct the results by the amount of the system loss before reporting the reference data.

A cylinder of approximately 10 ppm H_2S in nitrogen should be used to perform the recovery studies. Agreement between the reference method and the CEM should be within 5% or the system should be checked before initiating the Relative Accuracy testing.

11.3.2.7.3 Portable H_2S CEMs -

In addition to RAA and gas cylinder evaluations a portable system may be used to assess the long term performance of all installed TRS CEMs.

The use of portable CEMs by Kraft pulp mills has increased over the last several years. Portable CEMs enable the source to measure regulated emissions while minimizing time and manpower expenditures required by the Federal Reference Methods. Portable CEMs allow real time monitoring and decisions on corrective actions to commence immediately. The real benefits and applications of portable CEMs are:

- Stratification testing before permanently mounting CEMs on stacks or ducts;
- Parallel monitoring during periods of questionable operation by regulated CEMs;
- Diagnostic tool to check accuracy of installed CEMs and control equipment malfunction; and
- Compliance monitoring during "out-of-control" conditions of regulated CEMs.

11.3.2.8 Recordkeeping -

As part of a source quality assurance program, the following records associated with the continuous emission monitoring system should be maintained. They are:

- Monitor Logbook;
- Calibration Forms;
- Precision Assessment Forms;
- Audit Forms; and
- Strip Charts and Daily Computer Printouts.

Each of these records is discussed below.

11.3.2.8.1 Logbooks -

An instrument logbook should be maintained at the monitoring site by the Instrument Specialist. All activities related to the CEMs (maintenance, calibration, etc.) should be recorded on the logbook form, as illustrated in Table 11.7. Each entry in the logbook should include the date, a brief description of the activity, and the individual's initials.

If corrective action is needed, then the operator completes a TRS CEM Problem Communication Memo as illustrated in Table 11.8. This is then submitted to the CEM QA Coordinator or the CEM Supervisor for corrective action. The CEM QA Coordinator should maintain these records chronologically in a 3-ring binder. This provides documentation on when a problem was first detected and the need for corrective action to resolve the problem.

11.3.2.8.2 Calibration Forms -

Each time a calibration is performed the Instrument Specialist completes the Precision Calculation Form, as illustrated in Table 7.9. The form documents when calibrations are conducted and whether adjustments were made. The completed form is submitted to the CEM QA Coordinator who maintains a chronological record in a 3-ring binder.

TABLE 11.7
TOTAL REDUCED SULFUR
CONTINUOUS EMISSION MONITORING
SYSTEM LOGBOOK

DATE	ACTIVITIES OR MAINTENANCE	BY

TABLE 11.8
TOTAL REDUCED SULFUR
CEMS PROBLEM COMMUNICATION MEMO

From:______________________________

To:______________________________ Date:__________

Problem Definition & Recommendation__________________________

Signed____________________

Corrective Action Taken______________________________

Completion Date________________ Signed__________________

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TABLE 11.9
TOTAL REDUCED SULFUR
PRECISION CALCULATION FORM

PERIOD____________________ PARAMETER____________________

UNITS____________________

Date	CEMS Measured Conc. (Y_i)	Precision Check Conc. (X_i)	Percent Difference (d_i)	Date	CEMS Measured Conc. (Y_i)	Precision Check Conc. (X_i)	Percent Difference (d_i)
				n=		d_i =	

$d_i = Y_i - X_i$

11.3.2.8.3 Precision Assessment Forms -

An assessment of the CEMS precision is made by the CEM QA Coordinator each quarter. The precision calculations are performed using the form shown previously. The completed forms should be maintained by the CEM Supervisor and available for review.

11.3.2.8.4 Audit Forms -

As discussed earlier, a corporate self-audit should be conducted quarterly by the CEM QA Coordinator. Records of the quarterly audits should be maintained at the corporate offices by the Assistant Program Manager. The audit records would include the accuracy calculation forms and any notes or comments about the audit.

11.4 CONTROL AGENCY QUALITY ASSURANCE/QUALITY CONTROL ACTIVITIES

11.4.1 INTRODUCTION

Control agency quality assurance/quality control (QA/QC) activities are an integral part of an inspection program as outlined in Chapter 4. QA/QC activities for agency personnel involve all aspects of the phase and level compliance program. As discussed in Chapter 4, the phase process was administrative activities associated with the initial application and certification of the installed TRS CEM system. Figure 11.8 illustrates the three tiers associated with the phase process.

Phase I
Phase II
Phase III

Figure 11.8. Control Agency Phase Diagram

After completion of phase III, the level approach begins. Similar to the phase approach, the level approach has four tiers, as illustrated in Figure 11.9.

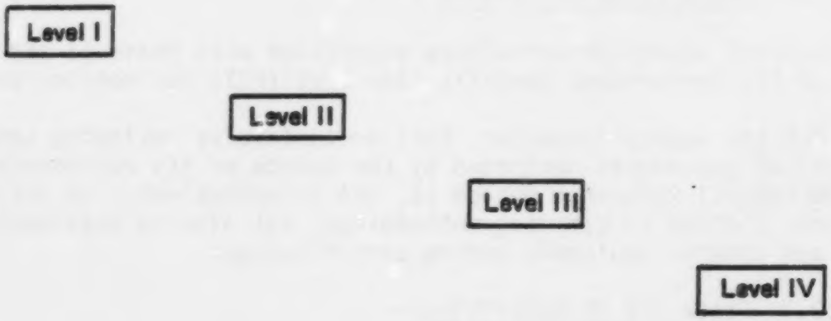

Figure 11.9. Control Agency Level Diagram

The phase and level audit procedure have been designed so that each activity indicates whether or not the CEM system has achieved the necessary level of compliance before starting the next phase.

Consequently, control agency QA activities are a major part of a source CEM program; from initial installation through performance certification to continuous compliance.

11.4.2 Control Agency QA Activities Involving the Phase Program

The phase process were administrative activities involved with initial CEM system application, performance testing and final approval. The type of activities at each phase are:

Phase I - Control agency initial approval of CEM application as required through the source permit;

Phase II - Control agency observation of Performance Specification Testing (PST) of the installed CEM system; and

Phase III- Control agency review of the PST report, with final approval or disapproval.

11.4.2.1 Phase I QA Activities -

Under Phase I, the control agency is ensuring that the source TRS CEM program meets all regulatory requirements. In particular, control agency QA/QC activities, at this level, involve implementation of

- Management Control System (MCS);
- Standard Operating Procedure Manual (SOP); and
- Source Quality Assurance (QA) Program within the permit.

11.4.2.2 Phase II QA Activities -

Control agency QA activities associated with Phase II involves observation of the Performance Specification Test (PST) for monitor certification.

For the agency inspector, this would involve reviewing sampling and analytical procedures performed by the source or its representative utilizing Federal Reference Method 16, 16A or equivalent. QA activities are not only limited to sampling methodology, but also to observation of process and control equipment during certification.

11.4.2.3 Phase III QA Activities -

Phase III QA activities consists of reviewing the Performance Specification Test report. The reviewer should make a determination of the acceptability of the test results and procedures. This determination should support a final approval, or disapproval of the Performance Specification Test Report.

To assist the agency in performing these QA activities during the phase program, several "Inspection" forms have been developed.

They are included in the supplement to this manual, entitled "Technical Assistance Document for Monitoring Total Reduced Sulfur (TRS) from Kraft Pulp Mills - Inspection Forms." The QA inspection forms which address the phase program are:

- o Federal Reference Method 16 Observation Checklist;
- o Federal Reference Method 16A Observation Checklist;
- o Performance Specification Test Report - General Review Checklist; and
- o Performance Specification Test Report - Detailed Review Checklist.

11.4.3 QA Activities Associated with Control Agency Level Program

The level program begins after completion of the phase program. QA activities associated with the level program extend from excess emission report review to stack test compliance determination. The type of activities at each level are:

Level I - Control agency records reviewing involves excess emission reports, previous inspection reports, source "working" file and permit review;

Level II - "Walk through" evaluation involving review of monitor recordkeeping (maintenance, monitor and control equipment logs), monitor fault indicator review, monitor internal zero/span check, strip chart review and electronic checks;

Level III - Evaluation of installed CEMs through external audit techniques involving neutral density filters for opacity monitors and gas cylinders/permeation tubes for gas monitors; and

Level IV - Comparative evaluation of installed CEMs through performance testing utilizing Federal Reference Methods or portable CEMs.

11.4.3.1 Level I QA Activities -

Level I control agency QA activities involve reviewing excess emission report for data accuracy and completeness. The inspector observes trends and exceedences as reported on the standardized excess emission report (Chapter 10). If discrepancies or inconsistances are noted, then quality control (QC) activities are initiated. To aid the inspector on the various QA activities associated with Level I, a checklist has been developed, entitled: "Excess Emission Report, Kraft Pulp Mills Reviewer's Checklist."

11.4.3.2 Level II QA Activities -

Level II agency QA activities are associated with evaluating the TRS CEM system at the regulated facility. The inspector performs a "walk through" QA inspection, beginning with records review and ending at the probe tip. The Level II QA activities involves review of recordkeeping and reporting activities, strip chart/data processor review, TRS CEM daily zero/span checks, remote display review, control equipment review and probe assembly evaluation. In essence, the QA "walk through" inspection correlates information from Level I review and comparing it to the Level II data.

To assist the inspector in the Level II QA activities, a Field Inspection Notebook has been developed as a supplement to this manual. The main objective of this notebook is to cover, in detail, the QA activities covering the level section of an Agency Inspection Program.

11.4.3.3 Level III QA Activities -

Level III QA activities involves a complete evaluation of the TRS CEM system by challenging it with certified pollutant gas concentrations Multiple concentration gases are injected, as close to the probe tip as possible, and the monitor responses is compared to the certified gas values. From this evaluation, a calibration error is determined. If the error falls outside calibration drift performance specification values, then the monitoring system is "out of control". This would initiate some form of corrective action by the regulated facility.

As discussed in Chapter 6.0, Generation of Standard Test Atmosphere, there are two techniques available to the inspector for generating known pollutant concentrations of total reduced sulfur (TRS) compounds. They are:

- Dynamic Calibration Systems; and

- Static Calibration Systems.

Dynamic calibration systems, utilizing either permeation tubes or gas cylinder dilution systems, provide the greatest flexibility in checking the precision and linearity of an installed TRS CEM system. Permeation tubes can be certified gravimetrically while reduced sulfur gases can be acquired at higher concentrations in gas cylinder, therefore circumventing many of the problems associated with low concentration reduced sulfur cylinder gases.

Different from dynamic audit systems, static audit systems do not involve diluting the gas concentration to a known value. Using a static audit system, the standard pollutant gas must be in the concentration range of the analyzer. This makes it very difficult, however, for the static audit system because NBS-SRM's are not available in the reduced sulfur compounds of interest. This limitation makes the dynamic calibration system more applicable as a QA activity.

11.4.3.3.1 Permeation Tube Audit System -

A permeation tube audit system consists of a clean air supply certifiable permeation tubes, constant temperature bath and a mixing chamber, as illustrated in Figure 11-10.

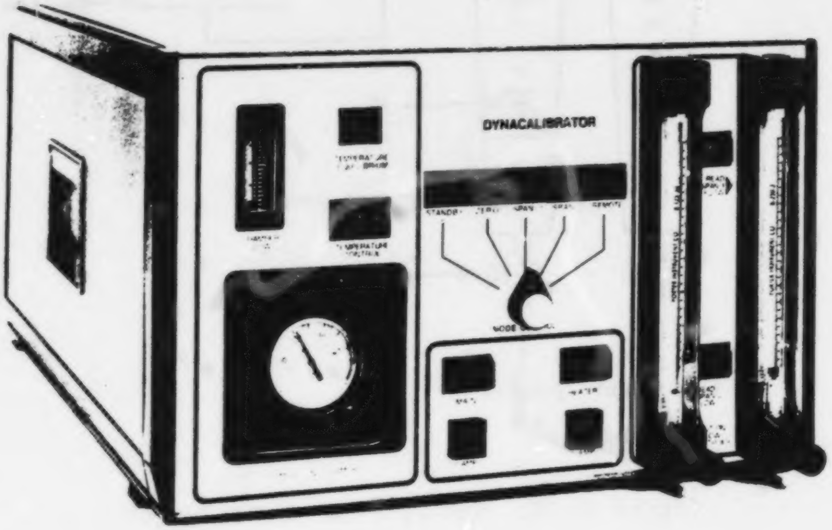

Figure 11.10. Typical Permeation Tube Audit System

By maintaining the flow constant across the tube and temperature of the bath constant, various concentrations of pollutant atmospheres can be generated by varying the diluent gas flow. This provides versatility as a QA auditing technique. Chapter 12, Equipment Selection, lists several manufacturers which sell commercially available portable permeation tube dilution systems.

11.4.3.3.2 Gas Cylinder Audit System -

The simplest and most economical QA audit system for providing a known concentration of pollutant gas to a monitoring system is the single dilution system, as illustrated in Figure 11.11.

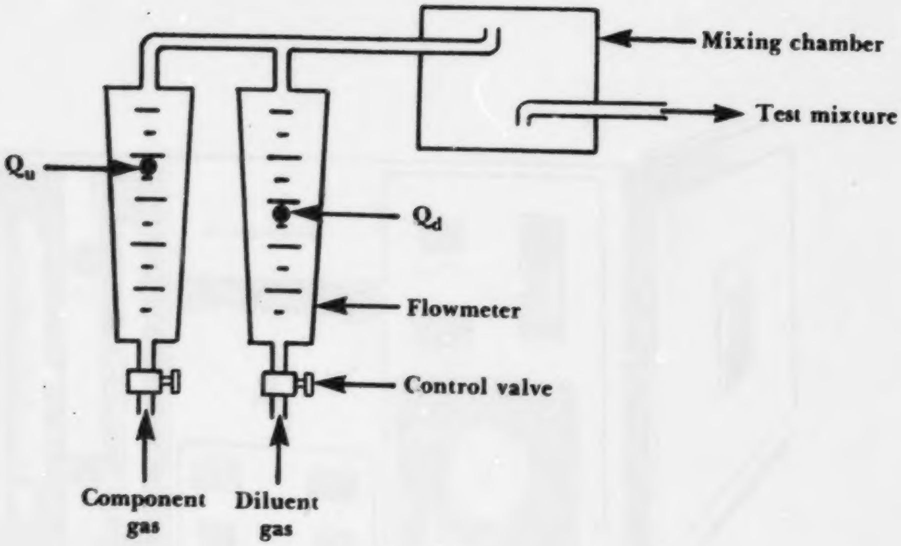

Figure 11.11. Gas Cylinder Audit System

In operation, a simple dilution system involves mixing a known concentration of pollutant gas with a diluent gas to provide a lesser known concentration of gas at the outlet. Utilizing the system in Figure 11.11, the outlet gas concentration can be calculated by the following equations:

$$C_u O_u = C_d (O_u + O_d)$$

where:

C_u = concentration of undiluted pollutant gas (ppm);
O_u = volumetric flow rate of undiluted pollutant gas (ml/min);
C_d = final concentration of diluted gas (ppm); and
O_d = volumetric flow rate of dilution gas (ml/min).

In this configuration, both the flows of the pollutant and dilution gases can be adjusted to provide a wide variation of pollutant gas concentrations. A 50:50 dilution is preferable, however, if matched rotameters are used. Likewise, flow rates can be verified by use of a bubble flow meter.

Utilizing this system, the auditor must be concerned with the calibration of the flow measuring devices used in the system to ensure an accurate production of pollutant gas is obtained. Figure 11.12 displays field use "matched" rotameters in a control agency gas cylinder audit system.

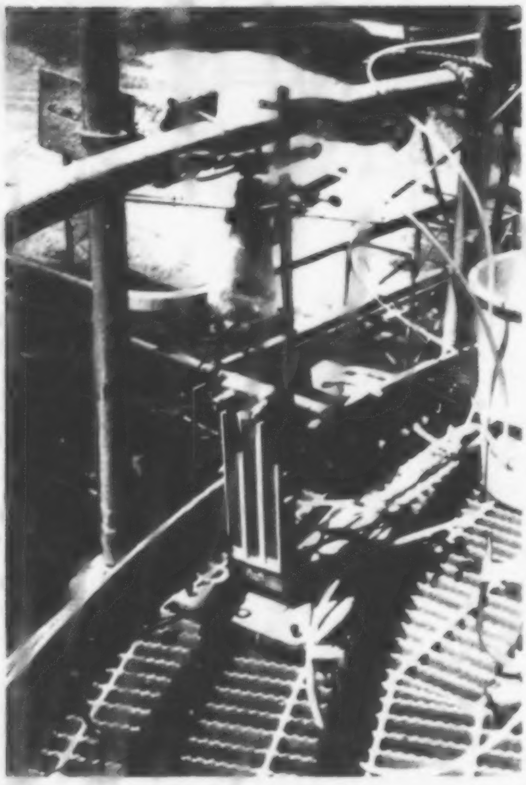

Figure 11.12. Use of Matched Rotameters In A Control Agency Gas Cylinder Audit System

Restricted or critical orifices have been used in one or both of the gas cylinder channels to provide an accurate flow measurement. Operated properly, critical orifices can lower the percent error associated with flow measurement technique. Figure 11.13 illustrated the use of a critical orifice in the pollutant gas line as a flow metering device.

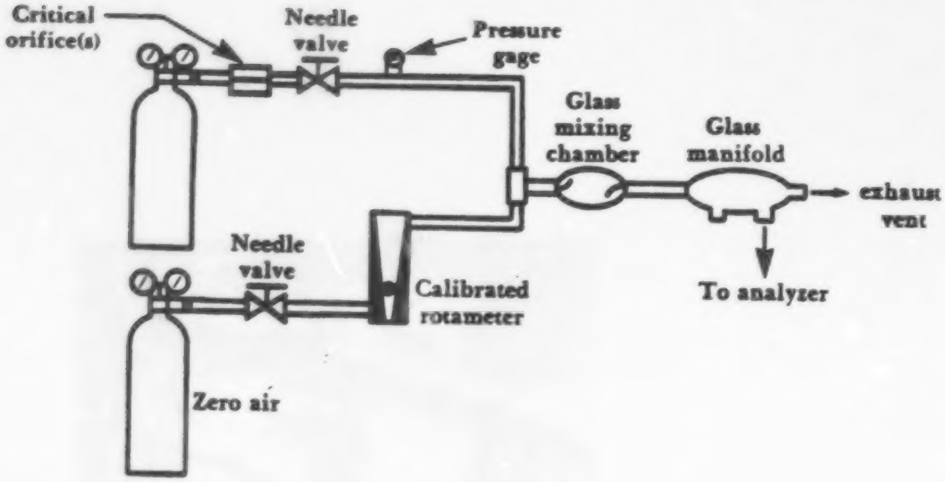
Critical orifice(s)
Needle valve
Pressure gage
Glass mixing chamber
Glass manifold
exhaust vent
Needle valve
Calibrated rotameter
To analyzer
Zero air

Figure 11.13. Use of A Critical Orifice in A Control Agency QA Audit System

In this configuration, the auditor need only to adjust the flow of the zero gas cylinder to produce various pollutant gas outputs, as calculated by the following equations:

$$C_u Q_u = C_d (Q_u + Q_d)$$

where:

C_u = concentration of undiluted pollutant in gas cylinder (ppm);
Q_u = rated flow of critical orifice (ml/min);
C_d = final concentration of diluted gas (ppm); and
Q_d = volumetric flowrate of dilution gas (ml/min).

Recently, the Research Triangle Institute developed a portable test atmosphere generating device. The device was designed to be:

- Compact, lightweight and self-contained;
- Limited operating controls; and
- Constructed so easy maintenance could be performed.

The portable test atmosphere generating device is based on the principle of gas phase dilution utilizing critical or restricted orifices as flow controllers. This technique is advantageous because higher concentrations of test cylinder mixtures are available, thus providing better gas stability. In addition, variable output of pollutant gas concentrations are easily generated by use of the toggle switches. This eliminates the need for flow measurements if the orifices are critical.

A pictorial illustration of the basic portable test atmosphere generating device is shown in Figure 11.14.

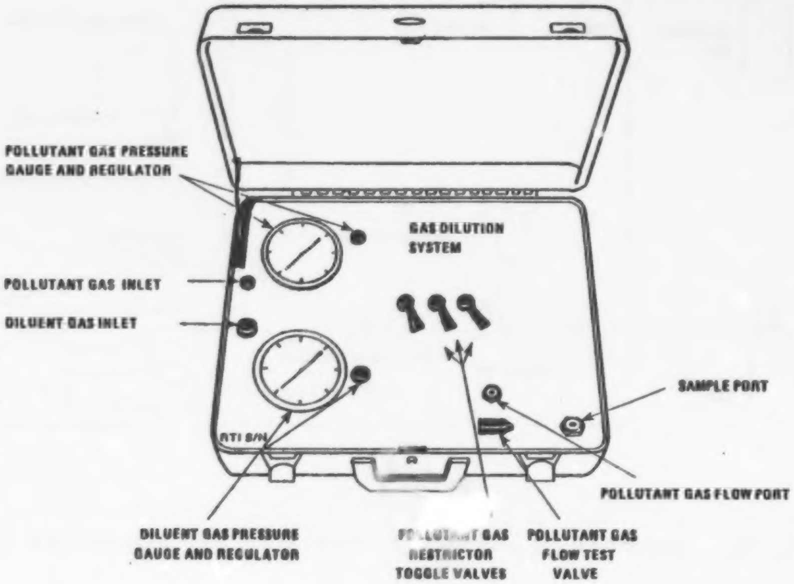
POLLUTANT GAS PRESSURE GAUGE AND REGULATOR
GAS DILUTION SYSTEM
POLLUTANT GAS INLET
DILUENT GAS INLET
SAMPLE PORT
RTI S/N
POLLUTANT GAS FLOW PORT
DILUENT GAS PRESSURE GAUGE AND REGULATOR
POLLUTANT GAS RESTRICTOR TOGGLE VALVES
POLLUTANT GAS FLOW TEST VALVE

Figure 11.14. Portable Test Atmosphere Generating Device.

The system provides a mechanism, whereby, quantities of the pollutant gas and diluent gas are mixed and exited out the sample port. The flow rate of each gas is controlled by maintaining a predetermined pressure drop across the orifices. Variation in exit gas concentration are obtained by switching the pollutant gas between three separate orifices.

In operation, the pollutant gas is introduced to the system from the pressurized cylinder through a bulkhead fitting, then flows through a porous plug particle filter to a pressure regulator. The pollutant gas then flows through the critical orifices to the mixing flask where dilution with zero air occurs. The critical orifices are so designed to give various flows so a multipoint calibration curves can be generated. Figure 11.15 illustrates the internal components of the portable test atmosphere generator.

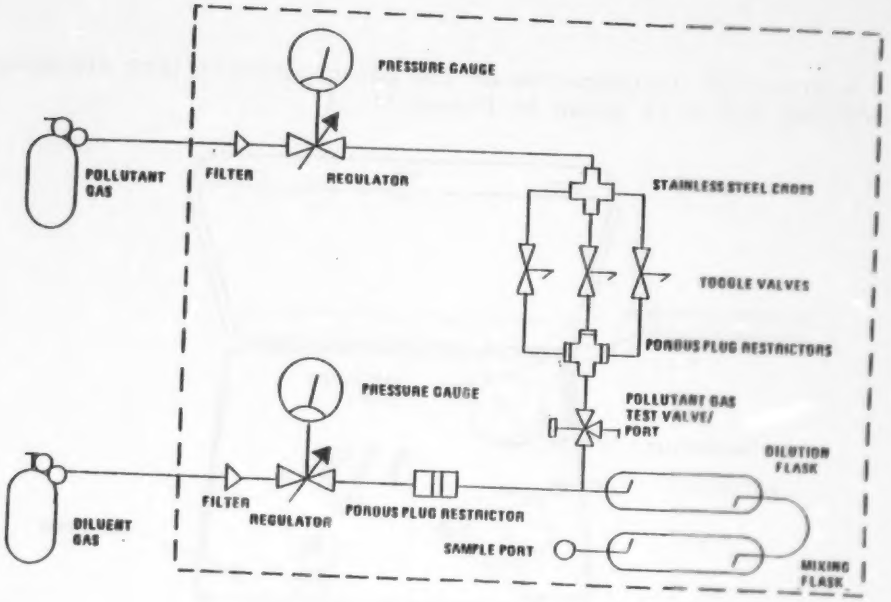
PRESSURE GAUGE
POLLUTANT GAS
FILTER
REGULATOR
STAINLESS STEEL CROSS
TOGGLE VALVES
POROUS PLUG RESTRICTORS
PRESSURE GAUGE
POLLUTANT GAS TEST VALVE/ PORT
DILUTION FLASK
FILTER
REGULATOR
POROUS PLUG RESTRICTOR
DILUENT GAS
SAMPLE PORT
MIXING FLASK

Figure 11.15. Internal Schematic of Portable Test Atmosphere Generator

The zero air (diluent gas) may be either cylinder air or generated from a zero air system. Like the pollutant gas, it also passes through a bulkhead fitting, a porous plug particulate filter, a pressure regulator and a flow restrictor before entering the mixing flask.

Seven (7) upscale concentrations can be generated by use of the toggle valves independently or in combination of each other.

11.4.3.4 Level IV QA Activities

Level IV QA activities involve recertification of the installed CEM system utilizing Performance Specification Test 5 and 3. The role of the control agency during this level is to observe the extraction and computation of emissions from the source during testing. At this time, additional "baselining" of the control equipment and continuous emission monitoring system can be performed. The QA forms used during Phase II, Performance Specification Test (PST) 5, are applicable during Level IV QA activities.

12.0 EQUIPMENT SELECTION

12.1 INTRODUCTION

The monitoring of total reduced sulfur compounds from Kraft Pulp Mills can be performed by either wet chemical or continuous emission monitoring instrumentation. As demonstrated in the previous Sections, each method exhibits both strengths and weaknesses. The wet chemical techniques are simplier to use, but care must be taken during all aspects of the procedures to insure an accurate "value".

Continuous emission monitors offer instantaneous analysis, but with limitations. In the past, criticism of CEM's have been that they are unreliable and perform poorly in a source environment. Indeed, many of the CEM's have performed well in the Laboratory; but once placed on or near a source, performance declines. This has been due, in part to the inexperience of source personnel in the operation and maintenance of the CEM systems. Most available systems on the market perform with the EPA's Performance Specification guidelines when a committment by the source is made to properly maintain the monitoring system. Recent data indicates when a source lacks this committment to its monitoring program, performance declines. Even the best built monitors, however, without a good operation and maintenance program, do not provide the reliable data needed for complying with air pollution regulations. Especially with monitoring reduced sulfur compounnds, many of the analytical techniques require specialized training.

12.2 VENDOR LIST

The objective of this chapter is to provide a list of vendors to the reader to assist in the selection of a total reduced sulfur monitoring system, whether wet chemical or continuous. The list was compiled from trade literature, vendor fliers, trade shows and personnel contacts. As with any list, it is never complete and is always outdated due to manufacturers reorganizing. The lists are provided only as a guideline to equipment and monitor selection.

12.2.1 Gas Manufacturers

G C Industries, INC.
20361 Prairie St. Unit 4
Chatsworth, CA 91311
(818) 701-7072

Scott Environmental Technology, Inc.
Rt. 611
Plumsteadville, PA. 18949
(215) 766-8861

Ideal Gas Products
P.O. Box 709
Edison, N.J. 08818
(800) 225-1706

M G Scientific Gases
2460 Blvd. of the Generals
Valley Forge, PA 19482
(215) 630-5492

Matheson Gas Products, Inc.
30 Seaview Dr.
Secaucus, NJ 07094
(201) 867-4100

Scott-Martin, Inc.
2001-H Third St.
Riverside, CA. 92507
(714) 784-1240

Gas Manufacturers (continued)

VICI Metronics
2991 Corvin Dr.
Santa Clara, CA 95051
(408) 737-0550

Arco Industrial Gases
575 Mountain Avenue
Murray Hill, NJ 07974
(201) 464-8100

AlphaGaz
Box 149 Woods Road
Cambridge, Md. 21613
(301) 228-6400
1-800-638-1197

Ideal Gas Products
977 New Durham Road
Box 709
Edison, NJ 08818
(201) 287-8766

12.2.2 Oxygen Analyzers (O_2)

Dynatron, Inc.
Box 745
Wallingford, Ct. 06492
(203) 265-7121

Econics Corp.
540 Dakmond Parkway
Sunnyvale, CA 94086
(408)738-8500

Teledyne Analytical Instruments
Box 1580
City of Industry, CA 91749
(818) 961-9221

Whittaker Environmental Products
12626 Raaymer Street
North Hollywood, CA 91605
(818) 765-6622

Delta F. Corp.
Walnut Hill Park
Woburn, MA. 01801
(617) 915-6536

Westinghouse Electric Corp.
Combustion Control Division
Box 901
Orrville, DH 44667
(415) 837-4622

Milton Roy Co.
Hays Republic Division
4333 S. Ohio St.
Michigan City, IN 46360
(219)879-4441

Datatest, Inc.
6850 Hibbs Lane
Levittown, PA 19057
(215) 913-0668

Sybron Corp.
Analytical Products Division
221 Rivermoor St.
Boston, MA 02132
(617) 469-3300

Hague International
3 Adams Street
South Portland, ME 04106
(207) 799-7347

Cleaver-Brooks Division
Aqua-Chem. Inc.
Box 421
Milwaukee, WI 53201
(414) 962-0100

Environmental Products
12626 Raymer Street
North Holywood, CA 91605
(213) 765-6622

Environmental Measurement
Research Corporation
17 N. 32nd. St.
Billingtons, Montana 59101
(406) 252-4450

Neotronics N.A. Inc.
Box 370
Gainesville, Ga. 30503
(404)535-0600

Gas Manufacturers (continued)

Cosa Instrument Corp.
70 Oak Street
Norwood, NJ 07648
(201) 767-6600

Lear Siegler, Inc.
74 Inverness Dr.
Englewood, CO 80112
(303) 792-3300

Ametek/Thermox Instrument Division
150 Freeport Road
Pittsboro, Pa. 15238
(412) 828-9040

EXO Sensors, Inc.
1220-B Simon Circle
Anaheim, CA 92806
(714) 632-8289

Thermo Electron Corp.
108 South Street
Hopkinton, Mass. 01748
(617) 435-5321

Anarad, Inc.
534 E. Ortega St.
Santa Barbara, CA 93103
(805) 963-6583

Yokogawa Corporation of America
2 Dart Road
Shenandoah, Georgia 30265
(404) 253-7000

Yokogawa Corp. of America (YEW)
2 Dart Road
Shenandoah, Georgia 30265
(404) 253-7000

Teledyne - Hastings, Inc.
Newcombe Ave.
Hampton, VA 23669
(804) 732-6531

Infrared Industries
Instruments Division
Santa Barbara, CA
(805) 684-4181

Delphi Instruments, Inc.
3030 Red Hat Lane
Whittier, CA 90601
(213) 692-9021

Beckman Instruments
Process Instruments Division
2500 Harbor Blvd.
Fullerton, CA 92634
(714) 871-4848

Bendix Corporation
P. O. Drawer 831
Lewisburg, WV 24901
(304) 647-4358

Bailey Controls Company
29801 Euclid Ave.
Wickliffe, OH 44092
(216) 585-6818

Land Combustion Inc.
3392 Progress Drive, Suite E
Bensalem, PA 19020
(215) 244-1100

12.2.3 Hydrogen Sulfide Analyzers (H_2S)

Bitel Manufacturing
2835 Laguna Canton Rd.
Laguna Beach, CA 92652
(714) 494-2012

Texas Analytical Controls
4434 Bluebonnet Dr.
Stafford, TX 77477
(713) 491-4160

Teledyne Analytical Instruments
16830 Chestnut St.
City of Industry, CA 91749
(818) 961-9221

Delta F. Corp.
Walnut Hill Park
Woburn, MA 01801
(617) 935-6536

12.2.3 Hydrogen Sulfide Analyzers (H_2S) (contd.)

Neotronics N.A. Inc.
Box 370
Gainesville, Ga. 30503
(404) 535-0600

DuPont Company
Analytical Instruments Division
Concord Plaza
McKean Bldg.
Wilmington, DE 19898
(302) 772-5481

Interscan Corp.
P. O. Box 2496
21700 Nordhoff St.
Chatsworth, CA 91311
(818) 882-2331

Jerome Instruments Corporation
Old High School
P. O. Box 336 Hwy. 89A
Jerome, Arizona 86331
1-800-952-2566

Houston Atlas Inc.
9441 Baythorne Dr.
Houston, TX 77241
(713) 462-6116

Candel Industries Limited
9365 W. Sannich Rd. Box 2580
Sidney, B.C. Canada V8L-4C1
(604) 656-0156

Tracor Atlas, Inc.
9441 Baythorne Drive
Houston, Texas 77041
(713) 462-6116

Sierra Monitor Corporation
1050 K East Duane Avenue
Sunnyvale, CA 94086
(408) 746-0188

12.2.4 Condenser (Refrigerated Moisture)

Hankison Corporation
1000 Philadelphia St.
Cannonsburg, Pa. 15317

Deltech Engrg. Inc.
Century Park
P. O. Box 667
New Castle, DE 19720
(302) 328-1345

Gen Cable Apparatus Div.
5600 W. 88th Ave.
Westminister, CO 80030
(303) 427-3700

Howell Labs, Inc.
54 Harrison Rd.
Bridgton, ME 04009
(207) 647-3327

12.2.5 Pumps

KNF Neuberger, Inc.
P. O. Box 4060
Princeton, NJ 08540
(609) 799-4350

Cole-Parmer Instrument Co.
7425 North Oak Park Ave.
Chicago, Ill. 60648
(312) 647-0272

Air Dimensions, Inc.
P. O. Box 867
Lansdale, Pa. 19446
(215) 368-5060

Thomas Industries
1419 Illinois Ave.
Sheboygan, Wis. 53081
(414) 457-4891

Contamination Control, Inc.
Forty Foot and Tomlinson Rds.
Kulpsville, PA 19443
(215) 368-2200

Science Pump Corporation
1431 Ferry Ave.
Camden, N.J. 08104

12.2.6 Combustion Tube (Quartz) for Thermal Oxidation Oven

Class Craft, Inc.
Rt. 1, Box 83
Micanopy, Fl. 32667
(904) 466-3412

Southern Scientific
Rt. 1, Box 83
Micanopy, Fl. 32667
(904) 466-3412

Fisher Scientific Co.
535 Alpha Drive
Pittsburg, PA 15238
(412) 562-8543

Applied Test Systems, Inc.
348 New Castle Road
P. O. Box 1529
Butler, PA 16001
(412) 283-1212

12.2.7 Filter

Ferro Corp.
Electro Div.
P. O. Box 389
601 W. Commercial St.
E. Rochester, NY 14445
(716) 586-8770

BGI, Inc.
58 Guinan St.
Waltham, Mass. 02154
(617) 891-9380

Pall Trinity Micro Corp.
Rt. 281
Cortland, NY 13045
(607) 756-7535

Fisher Scientific Co.
585 Alpha Dr.
Pittsburgh, PA 15238
(412) 562-8543

Millipore Corp.
Ashby Rd.
Medford, MA 01730
(800) 225-1380

12.2.8 Scrubbers - Teflon Continuous & Batch SO_2

Savillex Corp.
5325 Highway 101
Minnetonka, MN 55343
(612) 938-7727

12.2.9 Thermal Oxidation Oven

Fisher Scientific Co.
585 Alpha Dr.
Pittsburgh, PA 15238
(412) 781-3400

Batson, Louis P. Co.
P. O. Box 3978
Greenville, SC 29608
(803) 242-5262

CEM Corp.
P. O. Box 9
Indian Trail, NC 28079
(704) 821-7015

Trent, Inc.
201 Leverington Ave.
Philadelphia, PA 19127
(215) 482-5000

Lydon Bros. Corp.
85 Zabriskie St/P.O. Box 708
Hackensack, NJ 07602
(210) 343-4334

Thermovation Engineering
P. O. Box 24211
Cleveland, OH 44124
(216) 291-1236

US Testing Co., Inc.
1415 Park Ave.
Hoboken, NJ 07030
(201) 792-2400

12.2.10 Air Bath for Teflon Permeation Tubes

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

U. S. Testing Co., Inc.
1415 Park Ave.
Hoboken, NJ 07430
(201) 792-2700

Metronics Associates, Inc.
3201 Porter Dr.
Stanford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

12.2.11 Aspirator (Teflon) and Aspirated Gas Sampler

Lockwood & McLorie, Inc.
P. O. Box 113
Horsham, PA 19044
(215) 675-8218

12.2.12 Dynamic Gas Analyzer Calibration

Vici Metronics
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Matheson Gas Products, Inc.
30 Seaview Dr. Box 1589
Secaucus, NJ 07094
(201) 867-4100

Exemplar Design Engineering, Inc.
4422 D Catlin Circle
Carpinteria, CA 93013
(805) 684-0527

Demaray Scientific
Instruments, Ltd.
S. E. 1122 Latah St.
Pullman, WA 99163

G. C. Industries
20361 Prairie Street
Unit #4
Chatsworth, CA 91311
(818) 701-7072

Gas Technologies
555 Green Pl.
Woodmere, NY 11598
(516) 873-6413

Science Pump Corp.
1431 Perry
Camden, N.J. 08104
(609) 963-7955

Teledyne Hastings Raydist
Box 1275
Hampton, Va. 23661
(804) 723-6531

Candel Industries Ltd.
Box 2580
Sidney, B.C., Canada V8L-4C1
(604) 656-0157

Enviro Electronic Services Inc. (EESI)
P. O. Box 452
Greenfield, IN 46140
(317) 462-2614

12.2.13 Gas Permeation Tubes

Kin-Tek Laboratories, Inc.
Drawer J
Texas City, TX 77590
(409) 945-4529

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

12.2.13 Gas Permeation Tubes (contd.)

Vici Metronics
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

G. C. Industries, Inc.
20361 Prairie St.
Unit #4
Chatsworth, CA 91311
(818) 701-7072

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Stanford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

12.2.14 Sample Conditioner Systems

Environmental Products
12626 Raymer St.
N. Hollywood, CA 91605
(213) 765-6622

Exemplar Design Engineering, Inc.
4422 D. Catlin Dr.
Carpinteria, CA 93013
(805) 684-0527

Thermo Electron Corp.
108 South Street
Hopkinton, Mass. 01748
(617) 435-5321

Anarad, Inc.
534 E. Ortega St.
Santa Barbara, CA 93103
(805) 963-6583

DuPont Company
Analytical Instruments Division
Concord Plaza
McKean Bldg.
Wilmington, DE 19898
(302) 772-5481

Lear Siegler, Inc.
74 Inverness Dr., East
Englewood, CO 80112
(303) 770-3300

Columbia Scientific Industries
P. O. Box 9908
Austin, TX 78766
(512) 258-5191

Candel Industries, Inc.
P. O. Box 2580
Sidney, B. C. V81 4C1
(604) 656-0157

Sampling Technology, Inc.
P. O. Box B Highway 80E
Waldron, Arkansas 72958

Analon
P. O. Box 416
S. Bedford St.
Burlington, MA 01803
(617) 272-9002

Carton Technology
P. O. Box 26818
San Diego, CA 92126
(619) 578-5040

Acurex
555 Clyde Ave.
P. O. Box 7555
Mountainview, CA 94039

Western Research
1313 44th Ave., N. E.
Calgary, Alberta, Canada T2E 6L5
(403) 276-8806

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709
(919) 541-6000

12.2.14 Sample Conditioner Systems (contd.)

KVB
18006 Skypark Blvd.
P. O. Box 19518
Irvine, CA 92714
(714) 250-6200

Environmental Measurement Research
Corporation (EMRC)
17 N. 32nd Street
Billings, Montana 59101
(406) 252-4450

Combustion Engineering (CE)
Process Analytics
P. O. Drawer 831
Lewisburg, West Virginia 24901
(304) 647-4358

12.2.15 Probes

Anarad, Inc.
534 E. Ortega St.
Santa Barbara, CA 93103
(805) 963-6583

Teledyne Analytical Instruments
168030 Chestnut St.
City of Industry, CA 91749
(213) 961-9221

DataTest
6850 Hibbs Lane
Levittown, PA 19057
(215) 943-0668

Acurex Corp.
555 Clyde Ave. Box 7555
Mountainview, CA 94039
(415) 964-3200

Lear Siegler, Inc.
74 Inverness Drive, East
Englewood, CO 80112
(303) 770-3300

Mott Metallurgical Corp.
Farmington Industrial Park
Farmington, Conn. 06032
(203) 677-7311

DuPont Company
Analytical Instruments Division
Concord Plaza
McKean Bldg.
Wilmington, DE 19898
(302) 772-5481

Western Research
1313 44th Ave., N.E.
Calgary, Alberta, Canada T2E 6L5
(403) 276-8806

Candel Industries
Box 2580
Sidney, B. C., Canada V8L 4C1
(604) 656-0157

12.2.16 Stack Testing Equipment (Impingers, Sampling Train, Meter Box Assembly)

Nutech Corp.
2806 Cheek Road
Durham, N. C. 27704
(919) 682-0402

Anderson Samplers, Inc.
4215-C Wendell Dr.
Atlanta, Ga. 30336
(404) 691-1910

Sierra/Misco Inc.
1825 Eastshore Highway
Berkeley, CA 94710
(415) 843-1382

Research Application Co.
P. O. Box 265
Cambridge, Mass. 21613
(301) 228-9505

12.2.16 Stack Testing Equipment (Impingers, Sampling Train, Meter Box Assembly) (contd.)

KVB Equipment Corp.
18006 Skypark Blvd.
P. O. Box 19518
Irvine, CA 92714

Lear Siegler, Inc.
74 Inverness Dr., East
Englewood, CO 80110
(303) 792-3300

NAPP, Inc.
8825 N. Lamar
Austin, TX 78753

Precision Scientific Co.
3737 W. Cortland St.
Chicago, Ill. 60647

Analytical Instrument Development, Inc.
Rt. 41 and Newark Road
Avondale, PA 19311
(215) 268-3181

Korz Instruments, Inc.
20 Village Square Box 849
Carmel Valley, CA 93924
(408) 659-3421

Savillex Corp.
5325 Highway 101
Minnetonka, Minn. 55343
(612) 934-4050

Western Research and Development
1313 44th Ave. NE
Calgary, Alberta, Canada T2E 6L5

Thomas Scientific
Vine St. at 3rd, Box 779
Philadelphia, PA 19105
(215) 574-4500

Acurex Corp.
Energy & Environmental Division
485 Clyde Ave.
Mt. View, CA 94042

12.2.17 Heat Trace Lines

Technical Heaters, Inc.
710 Jessie Street
San Fernando, CA 91340
(818)361-7185

Samuel Moore & Co.
(Dekoron Division)
Industrial Park
Mantua, OH 44255
(216)274-2276

12.2.18 Pressure Gauges and Manometers

Fisher Scientific Company
585 Alpha Drive
Pittsburgh, Pa. 15238
(412) 781-3400

Airco Welding Products
(Distributors in most states)

Matheson Gas Products
P.O. Box E
Lyndhurst, N.J. 07071
(201) 935-6660

12.2.19 Regulators

Linde Specialty Gases (Model CRB 330)

Airco Industrial Gases
Union Landing & River Rds.
Riverton, N. J. 08077
(609) 829-7878

Matheson Gas Products
P. O. Box E
Lyndhurst, N. J. 07071
(201) 935-6660

Ideal Gas products
P. O. Box 709
Edison, N. J. 08810
1-800-225-1706

12.2.20 Flowmeters, Rotameters

Aalborg Instruments & Controls
2 Melnick Dr.
Monsey, NY 10952
(914) 352-3171

Ametek Schutte & Koering Div.
2233 State Rd.
Cornwells Heights, PA 19020
(215) 639-0900

AquaMatic Inc.
2412 Grant Ave.
Rockford, IL 61103
(815) 964-9421

Blue White Industries
14931 Chestnut Street
Westminster, CA 92683
(714) 893-8529

12.2.21 Flowmeters, Mass

Brooks Instrument Div.
407 W. Vine St.
Hatfield, PA 19440
(215) 362-3500

Kurz Instruments Inc.
P.O. Box 849
Carmel Valley, CA 93924
(408) 659-3421

M. G. Scientific Gases
2460 Blvd. of the Generals
Valley Forge, PA 19482
(215) 630-5492

Texas Nuclear Corp.
P.O. Box 9267
Austin, TX 78766
(512) 836-0801

12.2.22 Pumps, Diaphragm

Air Dimensions Inc.
P.O. Box 867
Lansdale, PA 19446
(800) 423-6464

B.A. Bromley Inc.
340 Main St.
Springfield, MA 01105
(413) 736-4280

Blue White Industries
14931 Chestnut St.
Westminster, CA 92683
(714) 893-8529

Bran & Lubbe Inc.
512 Northgate Pkwy
Wheeling, IL 60090
(312) 520-0700

Capital Controls Co., Inc.
P.O. Box 211
Colmar, PA 18915
(215) 822-2901

Warren Rupp-Houdaille Inc.
800 N Main St.
Mansfield, OH 44905
(419) 524-8388

Chem-Tech Inti
92 Bolt St/PO Box 1476
Lowell, MA 01853
(617) 453-4020

Gorman-Rupp Co., The
305 Bowman St.
Mansfield, OH 44902
(419) 755-1011

ITT Marlow Pumps
P.O. Box 200
Midland Park, NJ 07432
(201) 444-6900

KNF Neuberger Inc.
P.O. Box 4060
Princeton, NJ 08540
(609) 799-4350

Mec O Matic Co., The
P.O. Box 43390
St. Paul, MN 55164
(612) 739-5330

Wisa Precision Pumps
235 W. First St.
Bayonne, NJ 07002
(201) 823-3694

12.2.22 Pumps, Diaphragm (contd.)

Wilden Pump & Eng. Co.
22069 Van Buren St.
Colton, CA 92324

Zimpro Inc.
Military Rd.
Rothschild, WI 54474
(715) 359-7211

12.2.23 Pumps, Sampling

Aerovironment Inc.
825 Myrtle Ave.
Monovia, CA 91016
(818) 357-9983

Air Dimensions Inc.
P.O. Box 867
Landsale, PA 19446
(800) 423-6464

Allweiler Pump Inc.
5410 Newport Ave., #40
Rolling Meadows, IL 60008
(312) 892-9194

Fluid Metering Inc.
29 Orchard St/PO Box 179
Oyster Bay, NY 11771
(516) 922-6050

Geo. Engineering Inc.
100 Ford Rd., Bldg. 3
Denville, NJ 07834
(201) 625-0700

Gillan Instrument Corp.
8 Dawes Hwy.
Wayne, NJ 07470
(201) 831-0440

Gilson Medical Electronics Inc.
3000 W. Beltline Hwy.
Middleton, WI 53562
(608) 836-1551

Precisionaire
235 W. First St.
Bayonne, NJ 07002
(201) 823-3699

BVS Inc.
Rt. 322 W. & Poplar Rd.
Honey Brook, PA 19344
(215) 273-2841

Barnant Co.
28W092 Commercial Ave.
Barrington, IL 60010
(312) 381-7050

Brailsford & Co., Inc.
670 Milton Rd.
Rye, NY 10580
(914) 967-1820

QED Environmental Systems
P.O. Box 7269
Ann Arbor, MI 48107
(313) 995-2547

Robbins & Myers Inc.
1345 Lagonda Ave.
Springfield, OH 45501
(513) 327-3553

Roth Pump Co.
P.O. Box 910
Rock Island, IL 61201
(309) 787-1791

Science Pump Corporation
1431 Ferry
Camden, NJ 08104
(609) 963-7955

Wisa Precision Pumps
235 W First St.
Bayonne, NJ 07002
(210) 823-3694

12.2.24 Valves, Metering

DCL Inc.
P.O. Box 125
Charlevoix, MI 49720
(616) 547-5600

M. G. Scientific Gases
2460 Blvd. of the Generals
Valley Forge, PA 19482
(215) 630-5492

12.2.24 Valves, Metering (contd.)

Hammel Dahl & Jamesbury Cntrls. Co.
175 Post Rd.
Warwich, RI 01888
(401) 781-6200

Vlier Engineering
P.O. Box 7269
Burbank, CA 91510
(818) 843-1922

12.2.25 Valves - Needle

Cajon Company
32550 Old South Miles Rd.
Solon, OH 44139
(216)248-0200

Hoke, Inc.
Tenakill Park
Cresskill, N.J. 07626
(201)568-9100

Fluorocarbon
P.O. Box 3640
(1432 S. Allec St.)
Anaheim, CA 92803
(714)956-7330

Malema Engineering Corp.
500 NE 25th St.
Pompano Beach, FL 33064
(305)942-0880

Mueller Steam Specialty
P.O. Box 1569
Lumberton, NC 28359
(919)738-8241

Nupro Company
4800 E. 345th St.
Willoughby, OH 44094
(216)951-7100

Whitney Research Tool Company
5679 Landregon St.
Oakland, CA 94662

Parker Hannifin Corp.
P.O. Box 4288
Huntsville, AL 35802
(205)881-2040

Scientific Systems Inc.
1120 W . College Ave.
State College, PA 16801
(814)234-7311

Vlier Engineering
PO Box 7269
Burbank, CA 91510
(818)843-1922

12.2.26 Carbon Dioxide and Carbon Monoxide Analyzers

Anarad Inc.
534 E. Ortega St.
Santa Barbara, California 93103
(805)963-6583

Datatest Inc.
6850 Hibbs Lane
Levittown, PA 19057
(215)943-0668

Lear Siegler, Inc.
74 Inverness Dr.
Englewood, CO 80112
(303)792-3300

Syconex Corp.
1504 Highland Ave.
Duarte, CA 91010-2831
(818)359-6648

Du Pont Company
Analytical Instruments Division
Concord Plaza
McKean Building
Wilmington, DE 19898
(302)772-5431

Measurex Corp.
One Results Way
Cupertino, California 95014
(408)255-1500

12.2.26 Carbon Dioxide and Carbon Monoxide Analyzers (contd.)

Teledyne Analytical Instruments
16830 Chestnut Street
City of Indsustry, CA 91749
(23)961-9221

Horiba Instruments Inc.
1021 Duryea Ave.
Irvine, CA 92714
(714)540-7874

Westinghouse Electric Corp.
Combustion Control Division
Box 901
Orrville, OH 44667
(415)837-4622
1-800-628-1200

Land Combustion
3392 Progress Dr. Ste E
Bensalem, PA 19020
(215)244-1100

Dynatron Inc.
Barnes Ind Park Box 745
Wallingford, CT 06492-5847
(203)265-7121

Econics Corp.
540 Dakmond Parkway
Sunnyvale, California 94086
(408) 738-8500

Beckman Industrial Corp.
2500 Harbor Blvd.
Fullerton, CA 92634
(714)871-4848

Infrared Industries Inc.
P.O. Box 989
Santa Barbara, CA 93102
(805)684-4181

Thermo Electron Corp.
Box 459
Waltham, MA 02254
(617)890-8700

CEA Instruments
16 Chestnut St.
Emerson, NJ 07630
(201)967-5660

Servomex
Analytical Products Division
Sybron Corporation
221 Rivermoor St.
Boston, MA 02132
(617)469-3300

Rosemount Analytical
Uniloc Division
2400 Barranca Road
P. O. Box 19521
Irvine, California 92714

12.2.27 Fittings

Crawford Fitting Company
29500 Solon Road
Solon, OH 44139
(216)248-4600

Fluorocarbon, Process Systems Div.
P.O. Box 3640
(1432 S. Allec St.)
Anaheim, CA 92803
(714)956-7330

Fluoroware, Inc.
Jonathan Industrial Center
Chaska, MN 55318
(612)448-3131

12.2.28 Flow Controllers

Brooks Instruments
407 W. Vine St.
Hatfield, PA 19440
(215)368-2000

Condyne Instruments Co.
4851 Del Monte Rd.
La Canada, CA 91011
(619)829-7878

12.2.29 Portable Gas Chromatographs

Byron Instruments Inc.
520 S. Harrington st., Dept. PED
Raleigh, NC 27601
(919)832-7501

HNU Systems Inc.
160 Charlemont St.
Newton, MA 02161
(617)964-6690

Tracor Atlas Inc.
9441 Baythorne Dr.
Houston, TX 77041
(713)462-6116

Varian Assoc/D-070
611 Hansen Way
Palo Alto, CA 94303
(415)493-4000

Xentech Inc.
6662 Hayvenhurst Ave.
Van Nuys, CA 91406
(818)787-7380

Horiba Instruments
1021 Duryea Avenue
Irvine, California 92714
(714) 540-7874

Hewlett-Packard
P.O. Box 10301 MS 20B3
Palo Alto, CA 94303
(415)857-5731

Microsensor Technology Inc.
47747 Warm Springs Blvd.
Fremont, CA 94539
(415)490-0900

Foxboro Analytical
Box 5449
South Norwalk, CT 06856
(203) 853-1616

Baseline Industries
P.O. Box 649
Lyons, Colorado 80540
(303)823-6661

Sentex Sensing Technology
553 Broad Avenue
Ridgefield, N.J. 07657

12.2.30 SO_2 Analyzers

Environmental Measurement Research
Corporation (EMRC)
17 N. 32nd Street
Billings, Montana 59101
(406)252-4450

Teledyne Analytical Instruments
16830 Chestnut St.
City of Industry, California 91749

Thermo Electron Corp.
108 South Street
Hopkinton, Mass. 01748
(617) 435-5321

Whittaker Environmental Products
12626 Raymer Street
North Hollywood, California 91605
(213)765-6622

Columbia Scientific Industries
P. O. Box 9908
Austin, Texas 78766
(512)258-5191

Candel Industries, Inc.
P. O. Box 2580
Sidney, B. C. V81 4C1
(604)656-0157

12.2.30 SO_2 Analyzers (contd.)

Anarad, Inc.
534 E. Ortega St.
Santa Barbara, CA 93103
(805) 963-6583

DuPont Company
Analytical Instruments Division
Concord Plaza
McKean Bldg.
Wilmington, DE 19898
(302) 772-5481

Lear Siegler, Inc.
74 Inverness Dr., East
Englewood, CO 80112
(303)770-3300

Acurex
555 Clyde Ave.
P.O. Box 7555
Mountainview, CA 94039

KVB Equipment Corp.
18006 Skypark Blvd.
P. O. Box 19518
Irvine, CA 92714
(714) 250-6200

Sampling Technology, Inc.
P. O. Box B Highway 80E
Waldron, Arkansas 72958

Analon
P. O. Box 416
S. Bedford St.
Burlington, MA 01803
(617)272-9002

Carlton Technology
P. O. Box 26818
San Diego, CA 92126
(619)578-5040

Western Research
1313 44th Ave., N.E.
Calgary, Alberta, Canada T2E 6L5
(403)276-8806

Monitor Labs Inc.
10180 Scripps Ranch Blvd.
San Diego, CA 92131
(619)578-5060

12.2.31 TRS CEM Systems

Anacon
P.O. Box 416
South Bedford Street
Burlington, MA 01803

Applied Automation, Inc.
Pawhuska Road
Bartlesville, OK 74004
(918)676-6141

Bendix Corporation
(New Conbustion Engineering)
Environmental & Process
  Instruments Division
P. O. Drawer 831
Lewisburg, WV 24901
(304)647-4358

Candel Industries Limited
9865 West Saanich Road
P. O. Box 2580
Sidney, B. C. Canada V8L-4C1
(604)656-0157

Thermo Electron Corp.
108 South Street
Hopkinton, Mass. 01748
(617)435-5321

III Barton Instruments
900 S., Turnbull Canyon Rd.
P. O. Box 1882
City of Industry, CA 91749

Lear Siegler, Inc.
74 Inverness Drive East
Englewood, CO 80110
(404)763-8003

Sampling Technology, Inc.
P. O. Box B
Waaldron, AR 72958

Theta Sensors, Inc.
17635-A Rowland St.
City of Industry, CA 91748
(213)965-1539

12.2.31 TRS CEM Systems (contd.)

Charlton Technology, Inc.
P. O. Box 26818
San Diego, CA 92126
(619)578-5040

Columbia Scientific
Industries Corporation
P. O. 9908
Austin, TX 78766
(800)531-5003
(512)257-5181 (in Texas)

Eitel Manufacturing, Inc.
2835 Laguna Canyon Road
Laguna Beach, CA 92651

Westinghouse Electric Corporation
Combustion Control Division
Box 901
Orrville, Ohio 44667
(216) 682-9010

Syconex Corporation
1504 Highland Avenue
Duarte, California 91010-2831
(818) 359-6648

Elf Technologies, Inc.
103 East 37th Street
New York, New York 10016

Datatest, Inc.
6850 Hibbs Lane
Levittown, PA 19057
(215) 943-0668

Tracor Atlas, Inc.
9441 Baythorne Dr.
Houston, TX 77041
(713)462-6116

Western Research
1313-44 Avenue North East
Calgary, Alberta
Canada T2E6L5
(403)276-8806

Environmental Measurement Research
Corporation (EMRC)
17 N. 32nd Street
Billings, Montana 59101
(406) 252-4450

Measurex Corporation
One Results Way
Cupertino, California 95014
(408) 255-1500

Horiba Instruments
1021 Duryea Avenue
Irvine, California 92714
(714) 540-7874

MDA Scientific, Inc.
1815 Elm Dale Avenue
Glenview, Illinois 60025-1394
1-800-323-2000

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